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Influence of Sorbent Physical Properties upon Reactivity with Sulfur Dioxide

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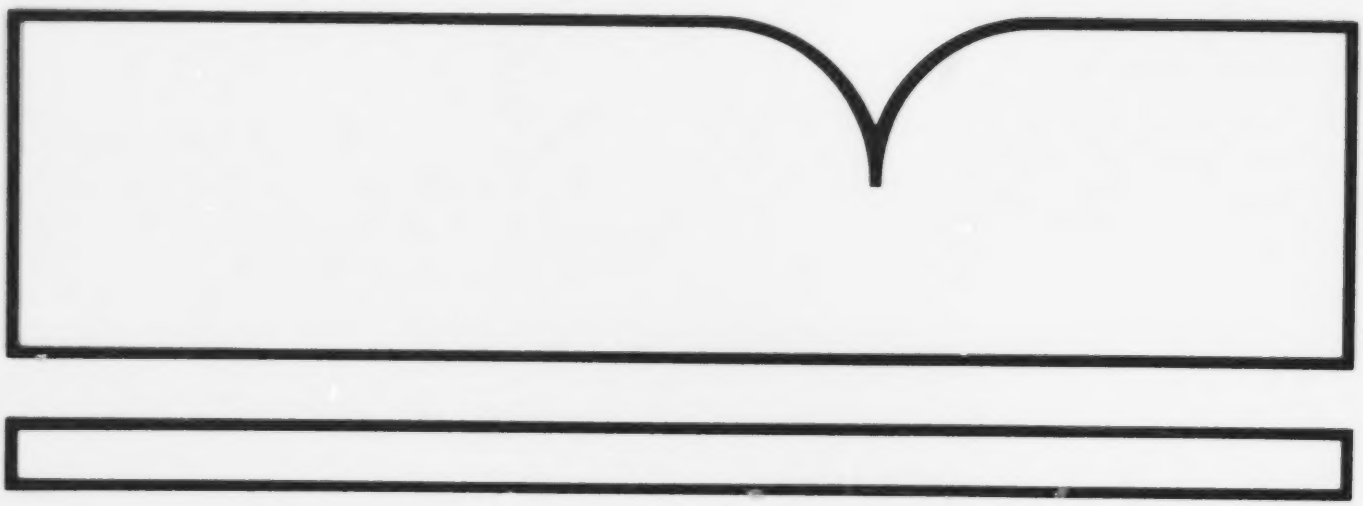

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THE INFLUENCE OF SORBENT PHYSICAL PROPERTIES UPON REACTIVITY WITH SULFUR DIOXIDE

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16. ABSTRACT The report gives results of sulfation behavior measured at 1000 and 1200 C for eight calcium oxide sorbents which were well characterized in terms of particle size, pore structure, and specific surface area. Sulfation results were compared with predictions of a simple mathematical model which applied the measured sorbent characteristics. The comparison, intended to provide direction for model development, suggests need for model improvement in areas such as global kinetics at short times, and accountability for changes in structure due to sintering during sulfation. Subsequently, the effects of the high temperatures on the surface areas of the sorbents in the absence of sulfation were also determined. Surface areas were marginally higher for the larger sorbents at 1000 C injection; but, in general, no correlation between particle size and surface area loss could be found. Surface area decay was shown to be very rapid in the first 200 ms, and subsequently very slow. Differences between carbonate and hydrate sorbents' reactivities were investigated using aerodynamically size-classified materials: hydrates were found more reactive on an equal prereactor size basis. Also, no thermal comminution of the hydrate particles was noted within the high temperature environment. Thus, the superiority of hydrates cannot be explained in terms of fragmentation upon firing.

17. KEY WORDS AND DOCUMENT ANALYSIS

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ABSTRACT

Sulfation behavior was measured at 1000 and 1200°C for eight calcium oxide sorbents which were well characterized in terms of particle size, pore structure, and specific surface area. Sulfation results were compared with predictions of a simple mathematical model which applied the measured sorbent characteristics. The comparisons, intended to provide direction for model development, suggest need for model improvement in areas such as global kinetics at short times, and accountability for changes in structure due to sintering during sulfation.

Subsequently, the effects of the high temperatures on the surface areas of the sorbents in the absence of sulfation were also determined. Surface areas were marginally higher for the larger sorbents after 1000°C injection, but, in general, no correlation between particle size and surface area loss could be found. Surface area decay was shown to be very rapid in the first 200 ms, and subsequently very slow.

Differences between carbonate and hydrate sorbents' reactivities were investigated using aerodynamically size-classified materials: Hydrates were more reactive on an equal pre-reactor size basis and no reduction in particle size occurred upon injection into the reactor.

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ABBREVIATIONS, SYMBOLS, AND TERMS

Å	angstrom unit, 10^{-8} cm
CaO	calcium oxide
^{o}C	degrees Celsius
Ca/S	calcium-to-sulfur molar ratio
CTT	controlled temperature tower furnace
diam	diameter
EDTA	ethylenediamine tetraacetic acid
ρ	porosity
g	gram
i.d.	inside diameter
ITR	isothermal reactor
K	thermodynamic temperature, Kelvin
kW	kilowatts
L	liter
m	meter
min	minute
MW 125	Marblewhite 125 limestone
μm	micron, 10^{-6} m
o.d.	outside diameter
ppm	parts per million (volume basis)
PCC	precipitated calcium carbonate
SEM	scanning electron microscopy
s	second
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SR	stoichiometric ratio (air/fuel) $\quad$ $(\text{air/fuel})_{\text{stoichiometric}}$
SR_1	stoichiometric ratio of ITR gas flame
SR_T	stoichiometric ratio of ITR flame and dilution air
STEM	scanning transmission electron microscopy
σ	standard deviation ($\pm$ σ = 67% confidence interval)
τ	residence time
UV	ultraviolet

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1.0 INTRODUCTION

1.1 Purpose and Scope

The purpose of this effort was to determine the influence of sorbent particle size on reactivity toward SO_2 in an isothermal environment. Two aspects of sorbent size were identified as important from current modeling efforts and general understanding. The first was the direct influence of particle size on the reactivities of constant surface area precalcined limes (Task 5). The second was the relationship between particle size and the relative reactivities of calcium hydroxides and calcium carbonates (Task 20).

The scope of the combined tasks covered was:

- Time-temperature measurements of SO_2 capture and surface area loss by eight size-classified precalcined sorbents.
- SO_2 capture measurements for three size-classified hydrated limes and two size-classified calcium carbonates.
- Cascade impactor sizing of size-classified hydrates and carbonates.
- Characterization of pertinent physical and chemical properties of all test materials.

1.2 Background

Dry calcium-based sorbent injection for SO_2 removal from flue gases is receiving considerable attention as the associated costs of conventional flue gas desulfurization (FGD) continue to increase (1,2). As a result, a wide variety of sorbents have been proposed and tested in various facilities (3,4,5) in attempts to identify materials and conditions which can make the dry sorbent injection process commercially viable. A key element in the process development is the use of modeling to generalize data between various test facilities and to extrapolate the data to full-scale.

Several models have been developed, or are under development, which describe the SO_2-lime reaction under specified conditions. These can be grouped under various classifications such as random pore models, grain models, pore tree models, distributed pore models, etc. (These names antedate the relatively recent studies of the SO_2-lime reaction. They have their origins in catalysis and coal combustion modeling and have only recently been applied to sorbent sulfation.) All of the existing models contain fundamental elements which either are poorly understood at the temperatures of interest or may only be estimated in order to provide a good fit with experimental data. Nonetheless, parametric sensitivity studies performed with numerical models can provide information which is useful in designing experiments in order to quantify important variables.

Mathematical models designed to predict the process of SO_2 capture by calcium-based sorbents suggest that sorbent reactivity is governed largely by two diffusional resistance terms and an additional constraint that arises from the interaction of the product with the sorbent structure (6). The first of these, pore diffusional resistance, dominates for large particles and is weakly dependent on surface area. The second term, product-layer diffusion, dominates for small particle diameters and is highly surface area dependent. Sulfation of the sorbents gives rise to a third impedance to reaction: the occlusion of the porous structure by the sulfate product.

Figure 1-1 illustrates these effects: it provides utilization vs. particle size estimates made by a grain model of sulfation for three different initial surface areas (m^2/g-CaO). This parametric sensitivity analysis demonstrates that at low surface areas reactivity is low and particle size has little influence. At moderate-to-high surface areas, however, there are three "regimes" of sorbent reactivity, including a distinct transitional regime between pore and product layer diffusional control. The importance of locating the transition lies in the fact that in its vicinity, only a small reduction in particle size is needed to gain a large increase in reactivity. Likewise, beyond the transition, further efforts at size reduction will produce only incremental gains in reactivity. This transition and leveling of the reactivity as size is reduced occurs

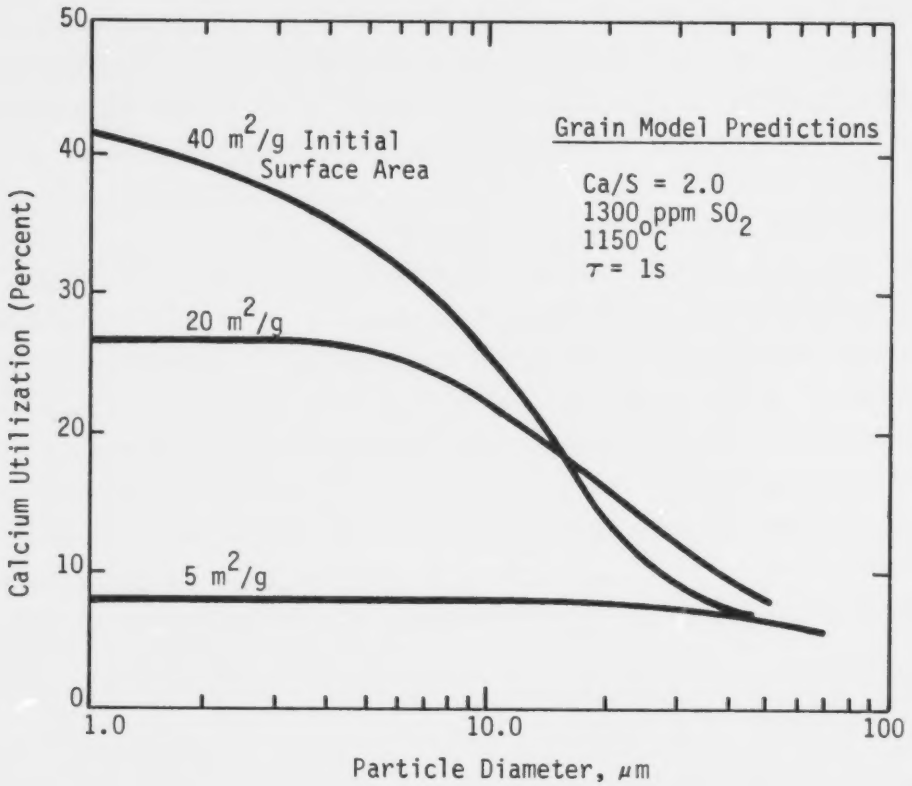

Figure 1-1. Sulfation model sensitivity analysis for the effects of particle size on sulfur capture by CaO.

essentially because the entire interior of the particle becomes uniformly accessible to SO_2. Under certain conditions, each of the major modeling formats (grain, pore-tree, distributed pore) will exhibit this behavior (6).

Recently, it has been recognized that calcium hydroxide sorbents as a group achieve higher utilizations than do limestones (7). One hypothesis for this in the framework of the preceding discussion is that it is a particle size effect; in general, calcium hydroxides are smaller than carbonates. This, however, is not entirely satisfactory because there is a wide range of sorbent reactivities both within and between each group which cannot be explained on the basis of particle size alone (6). Although particle size appears to be very important, Figure 1-2 shows that it is not always the sole factor for ranking utilization.

Experiences both with particle size measurements and with aerodynamic size classification have shown that particles in the micrometer size range tend to agglomerate. The energy necessary to disperse these agglomerates is often quite high. Conversely, during laboratory-scale furnace injection particle fragmentation has been observed over a range of conditions (5,8). This presents a second interesting hypothesis: differences in in-situ particle size, rather than pre-reactor size, may be responsible for the generally higher reactivities of hydroxides. This scenario also allows a plausible explanation for the differences in reactivity within these sorbent groups.

1.3 Approach

The tasks described herein addressed the issues outlined above, namely:

- direct determination of size influence on reactivity, and
- hydrate vs. carbonate reactivity.

The approach in the first task was to measure the reactivities of high surface area precalcines (prepared from calcium carbonate) having a wide

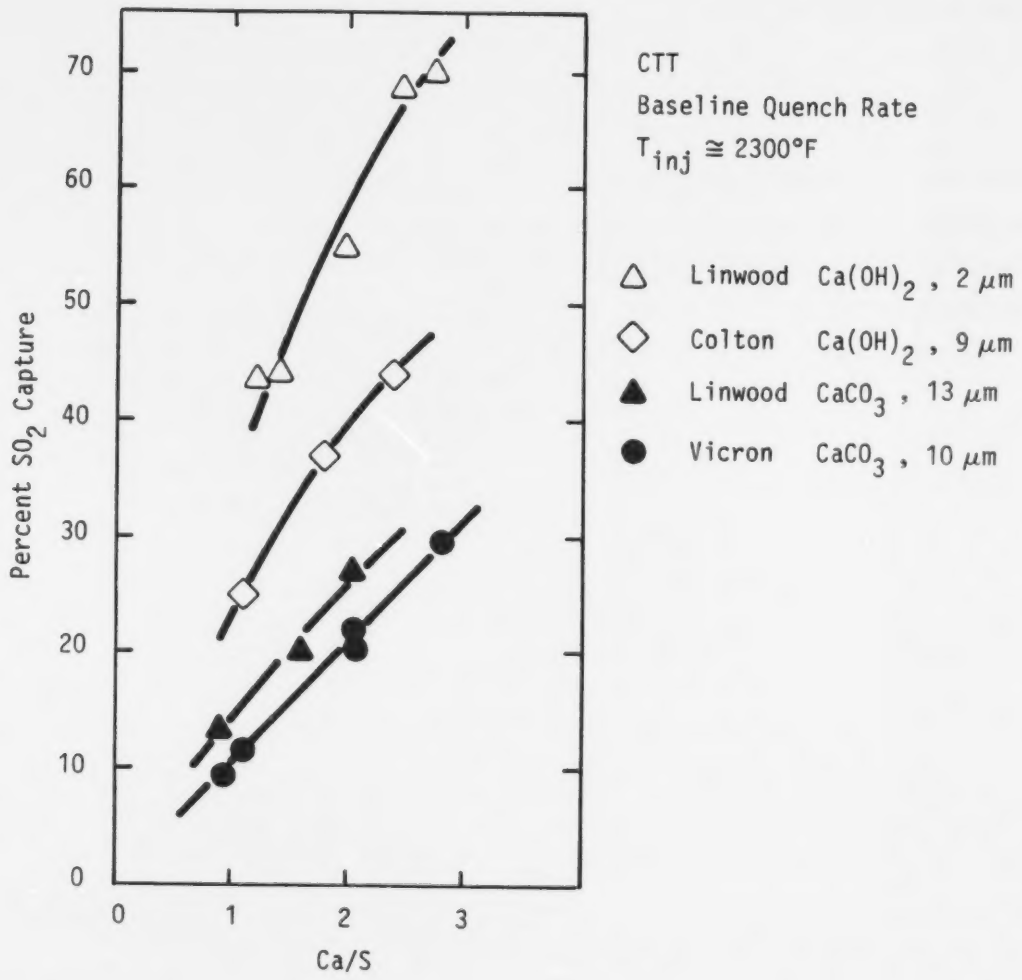

Figure 1-2. Comparison of sulfur capture capability for four different sorbent materials (6).

range of particle sizes. The precalcines had nearly constant initial surface areas of 25-32 m^2/g. Reactivity was determined as SO_2 capture vs. time at 1000°C and 1200°C so that experimental plots analogous to Figure 1-1 could be constructed.

In addition, solid samples were collected for surface area measurement. This was done to test the existing model assumptions about surface area loss and to provide input for further model development.

The approach to the second task was to measure SO_2 capture for a series of raw carbonates and hydrates which had been aerodynamically classified into narrow size cuts. Having compared the reactivities on an equal size basis, one size cut each (carbonate and hydrate) was tested for in-situ particle size using a Cascade impactor sampling system designed for this task.

2.0 CONCLUSIONS

The following conclusions can be drawn based upon the data and also upon the comparisons between the data and a grain model employing the intrinsic sulfation kinetics (labeled GR 84) measured by Borgwardt (4).

1. In the size range of 10-20 μm particle diameter, particle size and surface area have a weak effect on sorbent utilization.

2. For the initial surface areas of interest (25-30 m^2/g) at 1000°C, smaller particles were more completely utilized. However, the utilization was found to not depend entirely on particle size. Thus, the prediction of the grain model that the transition between pore and product layer diffusion would occur at 2-10 μm could not be verified.

3. Sintering in the absence of SO_2 is fast enough and severe enough at furnace temperatures to warrant accountability in sulfation models.

4. Differences in reactivity between hydrate and carbonate sorbents are not entirely due to a difference in their in-situ particle sizes.

3.0 RECOMMENDATIONS

Comparison of experimental results with model predictions suggest a rate of pore closure faster than can be accounted for by product layer development. This suggests that (1) sintering may be responsible for the observed behavior and may, in fact, be augmented by the formation of a $CaO-CaSO_4$ eutectic, or (2) that the sorbent structure may be different than the representation of the grain model, and that occlusion may occur more quickly. Several related experiments that are recommended here will help to resolve these points.

1. Examine changes in pore structure with time and temperature both in the presence of, and without, SO_2. This will help to explain the observed trends in sorbent utilization profiles, and will help select a sorbent structure format that matches physical reality.

2. Attempt to "profile" individual sulfated particles--that is, examine them using Auger Spectroscopy, electron microprobe, ESCA, or other analyses which may provide a measure of the penetration of sulfur species into individual particles of various sizes within the range of interest.

3. Measure the pore structure of "raw" materials calcined in-situ, both with and without SO_2. Data should be obtained, especially at short times, during pore structure development so that any differences between precalcined and in-situ calcined limes may be observed. Carefully precalcined stones of well-defined initial surface area, size, and pore structure are valuable for obtaining critical modeling information. However, such materials' structures may be artifacts of their preparation and, hence, may not represent what is truly occurring in stones calcined at high temperatures and short times. Quantifying any differences may be crucial to the final construction of a truly comprehensive model for dry lime injection and SO_2 sorption.

4.0 EXPERIMENTAL

The experimental effort for these tasks concentrated on gas-phase sampling of sulfur dioxide during sorbent injection into a laminar, isothermal, drop-tube furnace. Solid sampling was performed to provide surface area data as well as samples to check for sulfur balance closure. During the second task a technique was developed for cascade impactor sampling from the experimental furnace.

Experiments were, with one exception, carried out under isothermal conditions. Sampling techniques and system characterization were optimized to provide repeatability and rapid data collection. Solid sample collection followed previously established techniques (9). Gas-phase sampling techniques were essentially the same as those employed on bench-scale furnaces for prior EPA programs. Operating procedures for the experimental equipment are provided in the appendices.

4.1 Apparatus

The ITR is shown schematically in Figure 4-1. This reactor is a 21 kW, 1500°C three-zone Lindberg furnace. The heated zone is 0.9 m long and holds a 10-cm diameter reaction tube. Three independently controlled heating zones, separated by baffles, ensure that a flat temperature profile is maintained over the heated length. The large diameter of the reaction tube permits easy access for probing (bottom) and sorbent injection (top). Many of the ITR features were described in an earlier report (9) and are only summarized here.

The ITR is downfired by a precombustor assembly (Figure 4-2) which is coupled with a sliding burner. There are two main features to this assembly. First is the sliding burner. This is a premixed, water-cooled, flat-flame burner in a square stainless-steel chimney. By changing the burner position in the chimney, the downstream temperature (e.g., at the sorbent injector) can be varied independently of the burner stoichiometry and gas velocity.

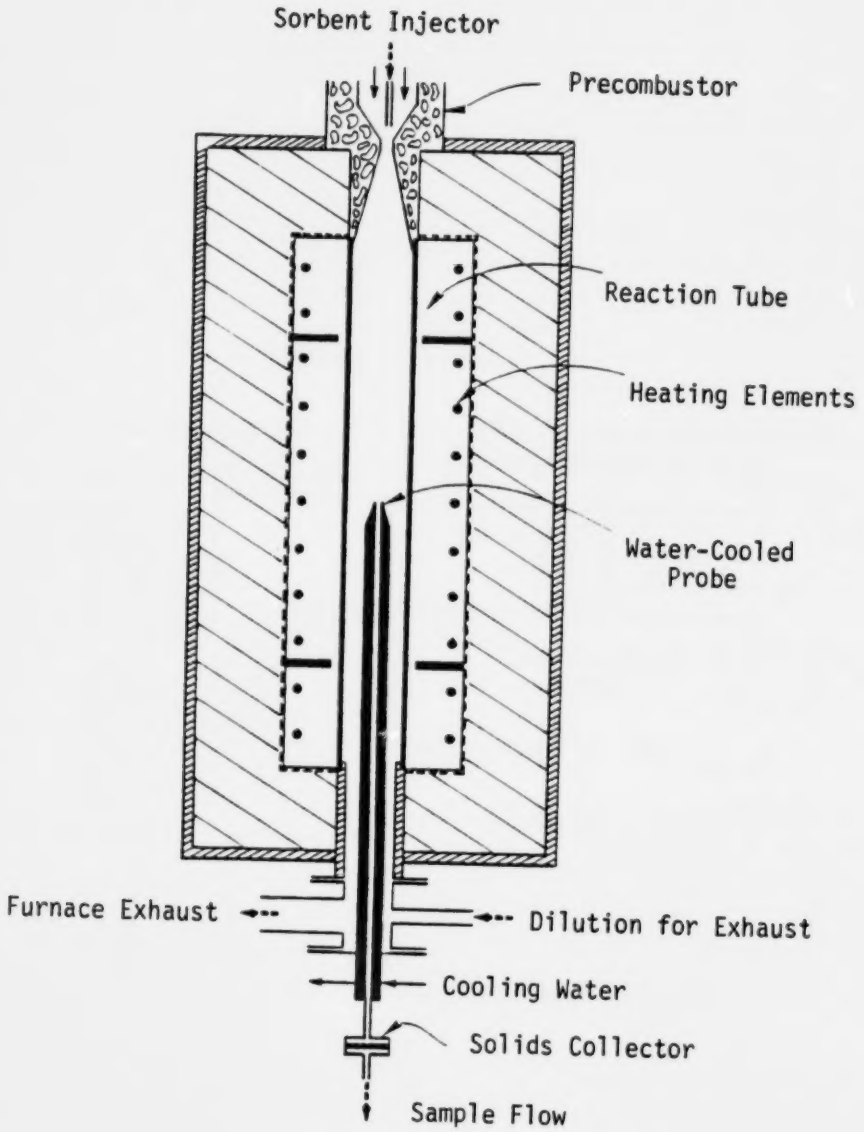

Figure 4-1. Schematic of the isothermal reactor (ITR). The solids collection probe (bottom) and lower portion of the precombustor (top) are also indicated.

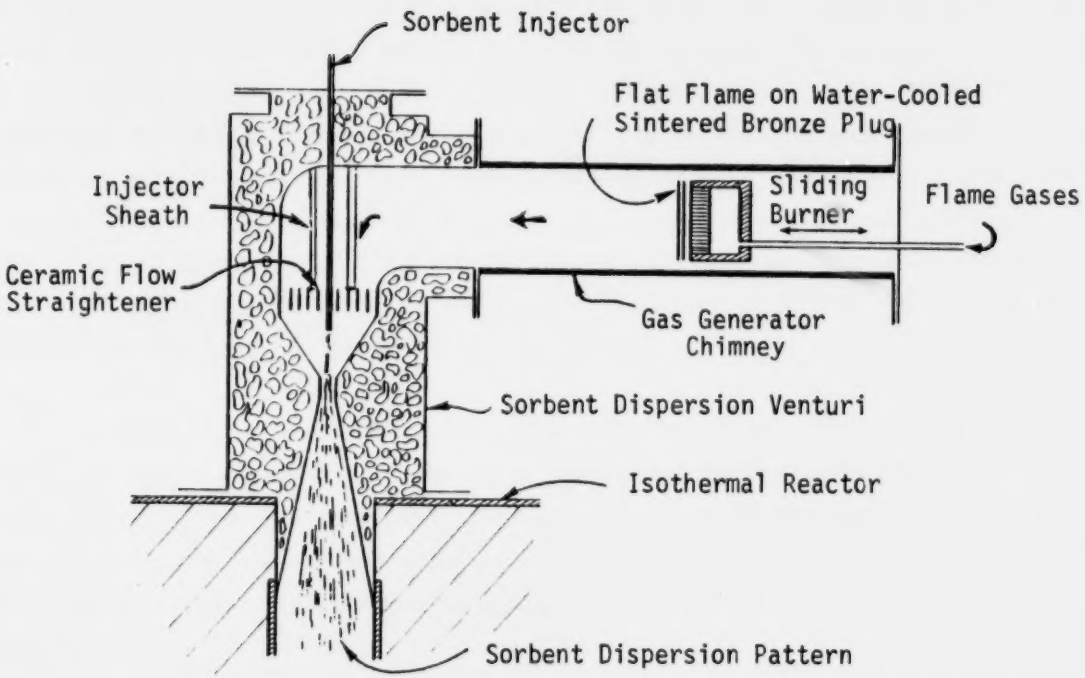

Figure 4-2. Schematic detail of the precombustor/sliding burner assembly. Typical sorbent injection is also indicated.

The second important feature is the venturi located just beyond the sorbent injector/flow straightener. As the burner gases pass by the sorbent injector, turbulence is induced by the contraction in diameter which reduces radial temperature gradients and improves sorbent dispersion and heat-up rates. Beyond the venturi throat is a 15° divergent section. The gradual divergence prevents backmixing and stabilizes a flat velocity profile.

Different probes were used for gas-phase and solids sampling. These are shown in Figure 4-3. Figure 4-3A shows the phase discrimination probe for gas sampling. This probe functions on the principle of inertial separation. A large volume of gas is drawn in through the probe tip. About 10 percent of that volume is redirected through a baffle to an outer plenum which leads to a gas analyzer (DuPont, non-dispersive UV absorption). Most of the solids continue directly through the center of the probe and are taken out in a water trap. The solid collection probe in Figure 4-3B is designed for isokinetic, or near-isokinetic operation. Sample is drawn into the top of the probe at approximately the reactor gas velocity. The sample is thermally quenched by the water-cooled walls and is drawn across an in-line filter mounted at the base of the probe.

Using either sampling probe, the sample stream proceeds to a water knock-out trap. This is followed by a continuous monitoring system (CMS) for flue gases. The CMS consists of a sample flow rotameter and SO_2, O_2, CO_2, and CO analyzers. These are used to monitor stoichiometry and to ensure that the reactor and sampling system operating conditions do not change during testing.

In-situ particle size measurements were made with the cascade impactor sampling system shown in Figure 4-4. The impactor was an Anderson Mark-II non-viable sampler. A dilution probe was used to extract the sample stream from the reactor and reduce the mass loading to a level compatible with the impactor while the impactor itself was kept at a constant 100°C in a drying oven. The eight-stage impactor provided size cuts between 0.4 and 10 μm at 28.3 L/s (1.0 scfm). The data were reduced following standard EPA procedures (10).

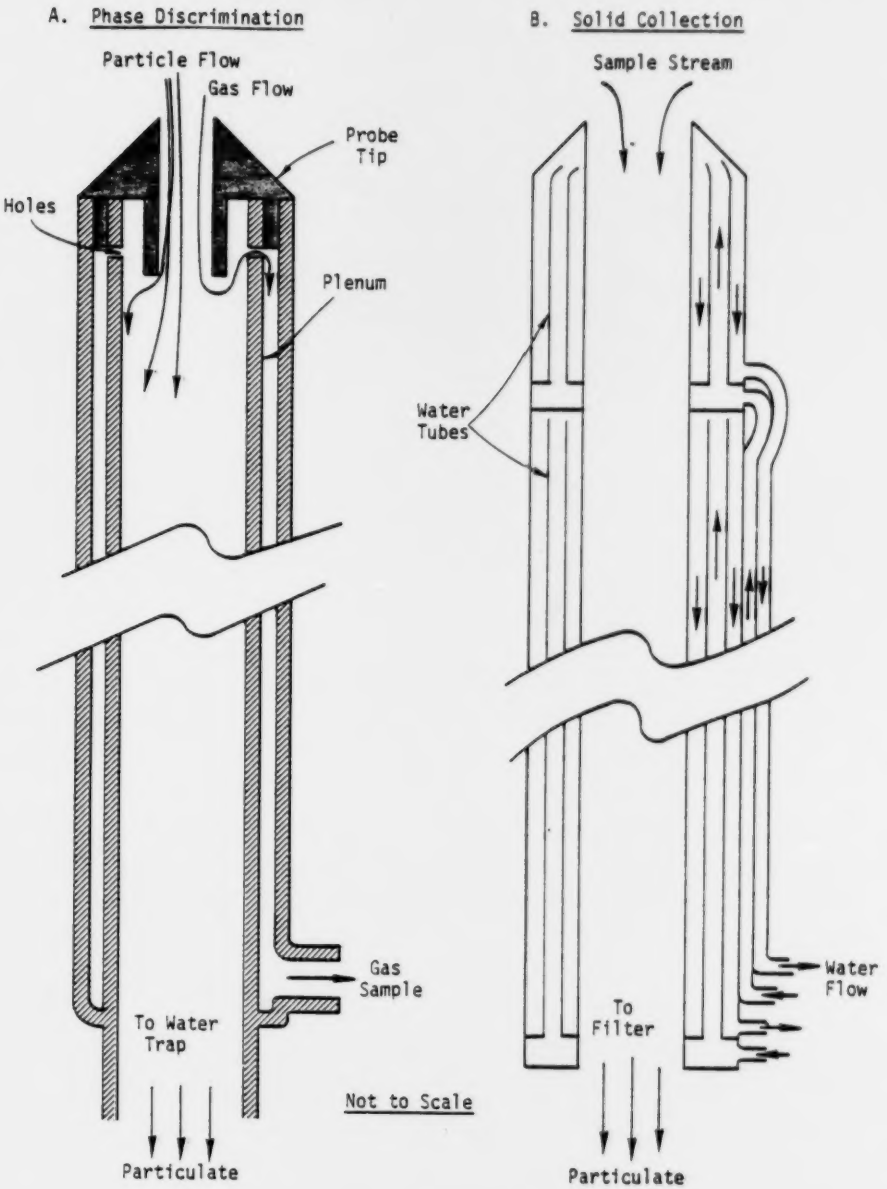

Figure 4-3. Sampling probes used in the ITR; A. Phase discrimination probe for gas sampling, B. Isokinetic solid collection probe with upper and lower cooling jackets.

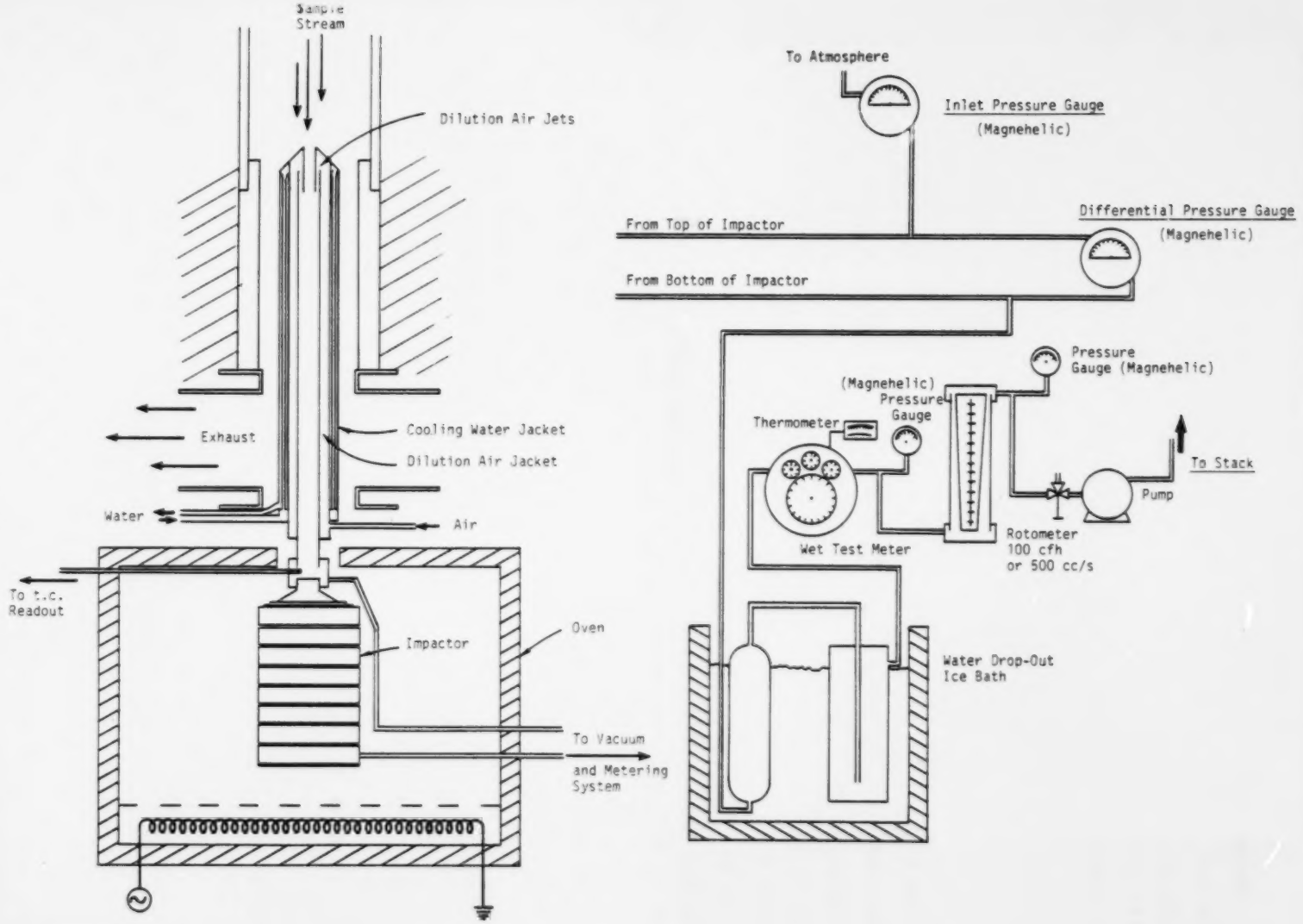

Figure 4-4. Schematic of the cascade impactor sampling system for the ITR.

4.2 Analytical Techniques

A host of analytical techniques were employed in this program. These were needed not only to provide reactivity data for the sorbents, but also as quality control checks on sorbent preparation and to define the physical parameters of the sorbents in sufficient detail for the modeling efforts. Since most of the analyses employed were standard techniques they will not be discussed in detail but are summarized below and in Table 4-1.

1. Particle Size Distribution

The principal technique used for particle size analysis was X-ray sedimentation (herein referred to as "Sedigraph," a trade name for the procedure as employed in this project by Micromeritics Corporation). This procedure operates on the principles of gravity sedimentation as defined by Stoke's law. The mass of particles settling from suspension at a given rate is measured by their attenuation of a collimated X-ray beam. The attenuation and the settling rate are converted into a cumulative plot of mass fraction vs. diameter. Electron microscopy (either SEM or STEM) was used to provide some of the particle sizes and also as a check on the Sedigraph results. In particular, the raw precipitated calcium carbonates were sized using micrographs provided by Pfizer Minerals and Pigments Division.

2. Specific Surface Area

Specific surface area was determined in-house on a Quantachrome Quantasorb unit. The analysis followed the BET model of nitrogen adsorption isotherms at 77 K.

3. Pore Size Distribution

Two techniques were assessed for pore size distribution measurements and porosity determinations. These were mercury

TABLE 4-1. SUMMARY OF ANALYTICAL TECHNIQUES

Parameter	Analysis	Purpose
Particle Size Distribution	Sedigraph (X-ray Sedimentation)	- Quality control check on starting materials. Input for model predictions.
Particle Size	Scanning electron microscopy (SEM) or scanning transmission electron microscopy (STEM)	- Particle size check for five materials.
Pore Size Distribution, Porosity Determination	Mercury intrusion porisimetry	- Input for model
Pore Size Distribution, Porosity Determination	N_2 adsorption-desorption isotherms	- Input for model
Specific Surface Area	N_2 absorption, BET technique	- Quality control check on calcined sorbents. Input for model.
SO_2 Concentration	DuPont SO_2 analyzer (non-dispersive UV absorption spectrometer)	- Sulfur capture, calcium utilization.
SO_2 Concentration	EPA Method 6 (gas scrubbing, barium titration)	- Verification of SO_2 span gas concentrations.
Sulfur Determination	Leco SC-32 (Instrumental total sulfur determination)	- Calcium utilization, solid samples.
Calcium Determination	ASTM D2795 (Chelometric titration)	- Calcium determination, solid samples
Carbon, Hydrogen Determination	Perkin Elmer 240B (Instrumental elemental analyzer)	- Quality control check, extent of calcination, hydration.

intrusion porisimetry and nitrogen desorption isotherm analysis. Both techniques assumed a right-circular-cylinder pore shape and provided pore sizes down to approximately 20 Å. Porosities for each sorbent were based upon the pore volume measured below 10 percent of the particle diameter. This is the approximate diameter of the smallest interparticle void spaces (interstitial spaces). For the precipitated calcium carbonates (Section 4.3.1) the porisimetry plots (Appendix E) show some overlap between interstitial and pore volumes. Some subjective interpretation was applied in order to estimate the pore volumes and porosities in these cases.

4. SO_2 Concentration

SO_2 concentrations were determined by UV-absorption. The absorption levels for the test gases were compared against those obtained with a calibrated span gas consisting of SO_2 in nitrogen. Calibration of the span gas was done titrametrically following EPA standard method 6.

5. Sulfur Determination

Total sulfur determinations in solid samples were obtained instrumentally on a Leco SC-32 Analyzer. This instrument combusts the sample in an oxygen rich environment to volatilize and oxidize the sulfur. The resulting gases then pass through platinum gauze which converts SO_3 to SO_2. The SO_2 is then determined photometrically and the results converted to weight-percent sulfur.

6. Calcium Determinations

Calcium was determined in solid samples following ASTM procedure D2795. The sample is digested in a buffered acid solution. This is then titrated with standardized EDTA. The method is highly specific to calcium.

7. Carbon, Hydrogen Determinations

Carbon and hydrogen (as CO_2 and H_2O) are determined in solid samples on a Perkin-Elmer 240B elemental analyzer. The sample is combusted in an oxygen-rich atmosphere. The resulting gases then pass through filters and thermal conductivity detectors which separately determine the H_2O and CO_2 content.

4.3 Experimental Conditions

4.3.1 Materials

Eight different sorbents were studied in the first task (Task 5) of this program. These are listed along with some of their physical properties in Table 4-2. All of these materials were obtained as raw calcium carbonates from Pfizer Minerals and Pigments Division. The first five were aerodynamically classified from Marblewhite 125 (MW 125), a commercial limestone. The latter three sorbents are precipitated calcium carbonates (PCC). The sorbents were all calcined to high surface areas in dry air at 700°C using a previously developed calcination procedure (11). Two of the MW 125 sorbents, 10 and 20 μm, were prepared by calcination to high surface area followed by sintering at 950°C for 30 minutes in flowing dry air. All of the sorbents were greater than 97 percent calcined.

Five raw sorbents (three hydrates and two carbonates) were studied in the second task (Task 20) of this program. Table 4-3 lists these along with their physical and chemical properties. The Linwood hydrates were obtained by aerodynamic classification of Linwood atmospheric hydrate. During aerodynamic classification some comminution of the hydrate was observed; however, it was possible to obtain distinct size classes, as shown by independent Sedigraph analysis in Appendix D. The Vicron sorbents were obtained likewise from Vicron 45-3, a commercial calcium carbonate.

TABLE 4-2. PHYSICAL PROPERTIES OF PRECALCINED LIME SORBENTS

Material	N_2-BET Area m^2/g	Mean Size Before Calcination μm	Pore Diameter at Max. Porosity Å	Porosity
20 μm	27	20	200	0.361
20 μm	12.5	20	270	0.37
10 μm	32	10	170	0.356
10 μm	11.7	10	270	0.37
Fines	27	~2[b]	170	0.388
Albacar[a]	25	2	-	0.47
Albagloss[a]	27	20.8	-	0.47
Multifex mm[a]	25	20.07	-	0.486

[a] Trademarks of Pfizer Minerals and Pigments Division

[b] By SEM

TABLE 4-3. PROPERTIES OF RAW SORBENTS

Sorbent	Mean Size (μm)	Wt-Percent Calcium
Linwood 2 μm	2.1 μm	50.2
Linwood 9.4 μm	9.4 μm	50.0
Linwood 30 μm	30.0 μm	46.0
Vicron 8.8 μm	8.8 μm	39.5
Vicron 18 μm	18 μm	40.4

TABLE 4-4. ISOTHERMAL REACTOR OPERATING CONDITIONS

Test	Fuel	Firing Rate kW (kBtu/hr)	SO_2 Conc. ppm (dry, 0% O_2)	SR_1	SR_T
Task 5	CH_4	4.6 (16)	4200	1.01	1.10
Task 20	CH_4	9.4 (32)	3000	1.05	1.20

4.3.2 Reactor Operating Conditions

The reactor operating conditions for both Task 5 and Task 20 are outlined in Table 4-4. In the table SR_1 is the air/fuel stoichiometric ratio of the flame and SR_T refers to the same value, but includes both the flame and the dilution air passed around its edge. During the surface area and cascade impactor sampling tests no SO_2 was added to the reactor.

5.0 RESULTS AND DISCUSSION

The results presented in this section are those which directly address the objectives of this combined-task program. Additional data are presented in the appendices.

5.1 Precalcine Sulfation Data

Time resolved SO_2-capture tests were performed with six high surface area precalcined sorbents at 1000°C and 1200°C. Three of these materials: 2 μm, 10 μm, and 20 μm, were prepared from aerodynamically classified Marblewhite 125 (MW 125), a commercial limestone. The remaining three were prepared from the precipitated calcium carbonates (PCC): Multifex MM, Albagloss, and Albacar 5970. Additional time-resolved tests were performed with two low surface area precalcines prepared from the 10 and 20 μm MW 125. Albacar and Albagloss precalcines were used in high-temperature injection tests to determine whether very fine sorbents are resistant to thermal deactivation.

The precalcines were utilized further in a parametric study of surface area loss. Time-resolved data are presented for the high surface area loss. Time-resolved data are presented for the high surface area 10 μm MW 125. The remaining samples were collected at a fixed "end of reactor" location.

5.1.1 High Surface Area Precalcines

Time-resolved sulfation data for the precalcines at 1000°C are shown in Figure 5-1. With the exception of the Albagloss precalcine, the majority of the sorbent reaction occurs within the first 250 ms after injection. Figure 5-2 shows similar data generated at 1200°C. Again, most of the sulfation occurs at very short times. Taken together, the two data sets exhibit the following behavior:

- In going from 1000°C to 1200°C the larger sized sorbents (20, 10, 2 μm) and the Albagloss either increased in utilization, or stayed

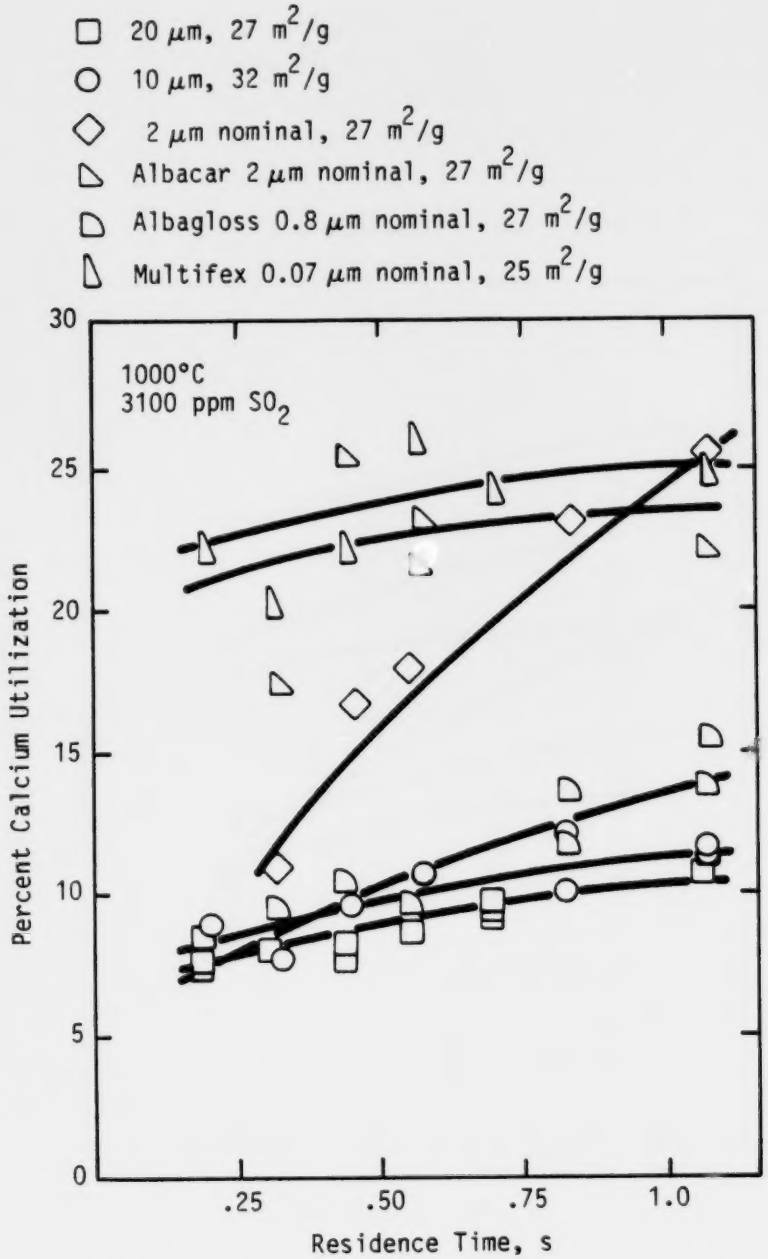

Figure 5-1. Isothermal reactivity of calcined sorbents at 1000°C in the EER isothermal reactor at Ca/S = 1.0.

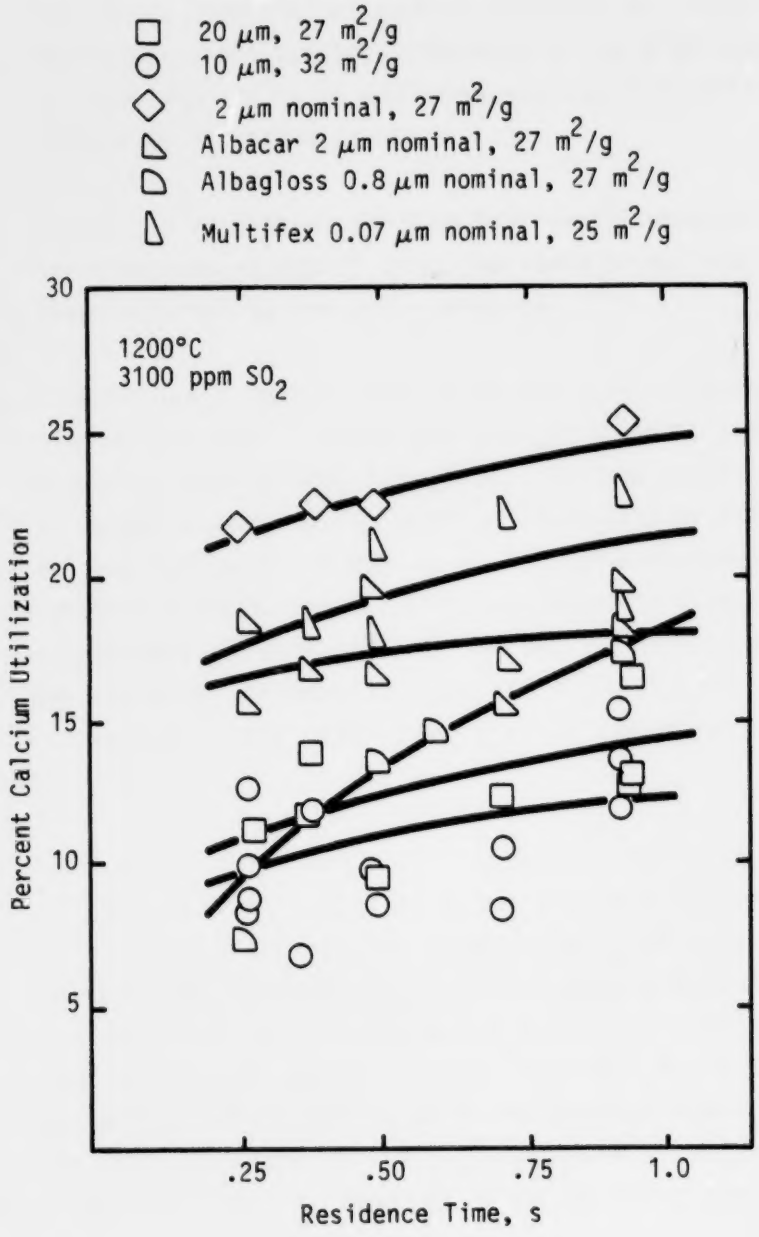

Figure 5-2. Isothermal reactivity of calcined sorbents at 1200°C in the EER isothermal reactor at Ca/S = 1.0.

the same. The smaller sorbent (Albacar, Multifex) showed a slight decrease in utilization. (Because of its high aspect ratio, there is some ambiguity in defining the correct particle size for the Albacar as discussed below).

- Two of the materials, the 2 μm Marblewhite precalcine at 1000^{o}C and the Albagloss at 1200^{o}C show a markedly higher reactivity at longer times relative to the other sorbents.

The Albacar has a needle-like structure with a diameter of 0.5-0.7 μm and a length of 2-4.5 μm. Thus, the Albacar presents a minimum dimension that is less than that of the Albagloss. The key question is whether the material is better represented in terms of reactivity by its nominal size as reported by the Sedigraph (2 μm) or by its minimum diameter (0.5-0.7 μm). Since the models predict that the size dependence is governed mainly by the relationship between the particle interior and its closest surface, then the 0.5-0.7 μm would be the more appropriate dimension for characterizing sulfation behavior. Both dimensions will be considered in analyzing size dependence.

The dependence of ultimate utilization on particle size is shown in Figure 5-3. The Albacar is plotted as two points to illustrate each of the interpretations of its size. The data support the conclusion that finer particle size promotes improved utilization at both temperatures. Direct use of the grain model against the data indicate that pore diffusion ceases constraining the process below 1-2 μm. The data do not clearly replicate this trend. Rather, there appears to be differences between the precalcines that are not fully characterized by the particle size, surface area, or pore size measurements. This is supported by the anomalous behavior noted above in Figures 5-1 and 5-2.

At 1200^{o}C the data generally show less variation in utilization with particle size. The grain model vastly overpredicts capture at this temperature which illustrates the necessity of including a sintering step in the calculation to correctly predict high temperature behavior. For both

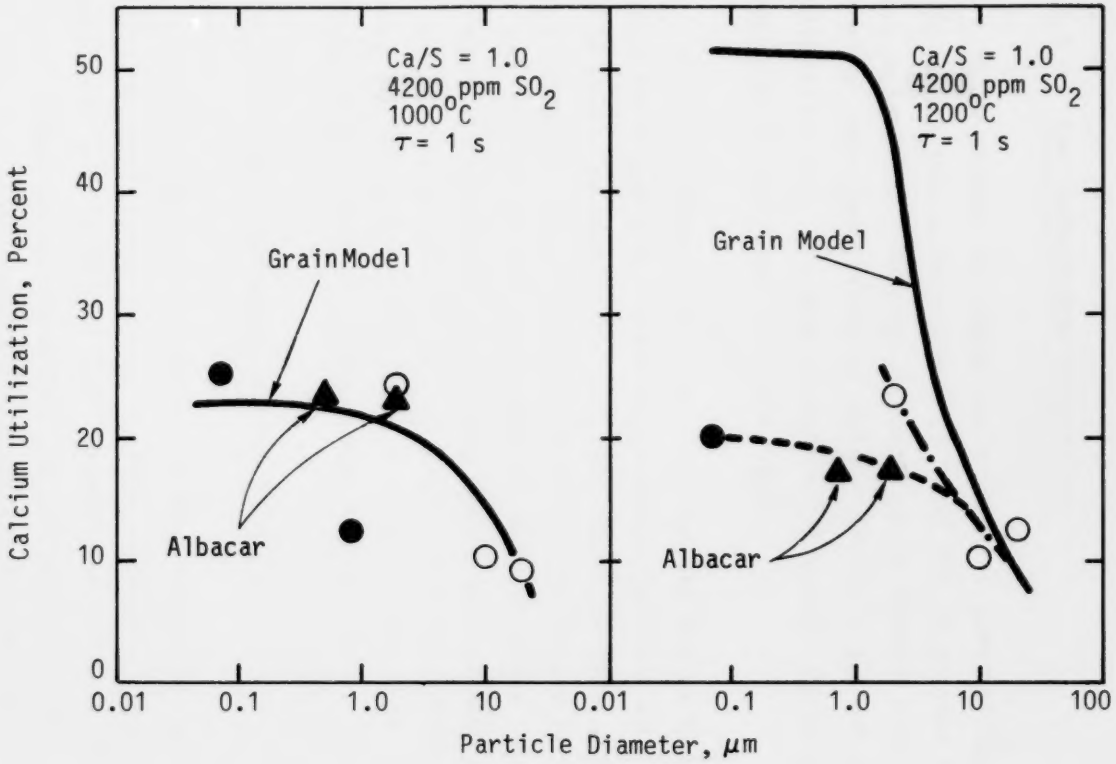

Figure 5-3. A summary of the sulfation vs. particle size data for precalcined materials. The solid lines are the grain model predictions. Solid symbols represent precipitated calcium carbonates, open symbols represent MW125.

1000 and 1200°C, there are sufficient uncontrolled differences between the sorbents (manifested as apparent data scatter) to prevent a verification of the grain model conclusion that pore resistance becomes insignificant below about 1 μm.

5.1.2 Low Surface Area Precalcines

In an attempt to reduce the effects of pore diffusion, two lower surface area precalcines were sintered at 950°C for 30 minutes to produce low surface area materials. Despite reductions in surface area from about 30 m^2/g to 12 m^2/g, the porosities of these materials did not change (see Table 4-2) indicating that the pore diameters increased. Mercury porosimetry analyses (Appendix E) confirmed this conclusion.

Time-resolved sulfation data for the low surface area precalcines are shown in Figure 5-4. Grain model predictions for each case are shown as the solid curves on each graph. In both cases the model again does a fair job of predicting the data. Capture for the two materials is quite similar in spite of the factor of two difference in particle size. More important, however, is that the measured SO_2-capture levels were reduced only slightly relative to the change in initial surface area. This confirmed another hypothesis put forth by the model, namely that as particle size increases, surface area becomes less a factor in determining reactivity.

5.1.3 High Temperature Sorbent Injection

Previous data on the effect of temperature on surface area indicate that sorbent reactivity should decline rapidly as injection temperature is increased beyond 1150°C (5). Nevertheless, faster reaction kinetics at the higher temperatures may offset the surface area loss. This might especially be true for small sorbent diameters where pore diffusion resistance is small and the magnitude of product-layer diffusion resistance is limited by the particle dimensions.

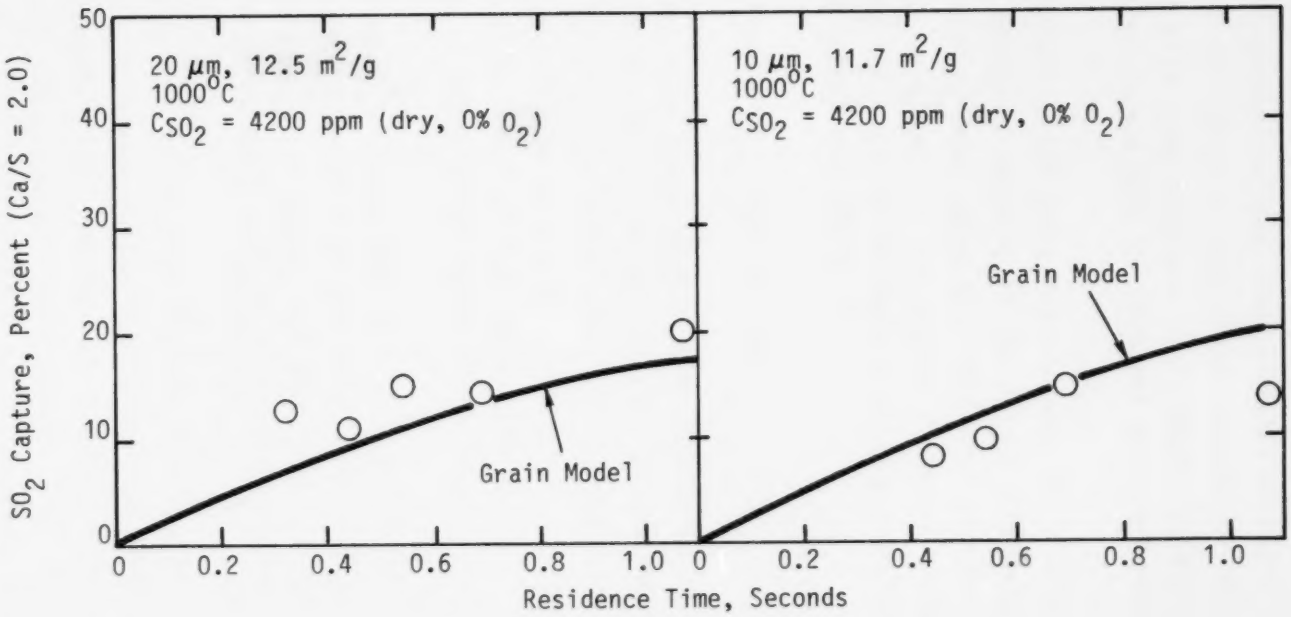

Figure 5-4. Time-resolved SO_2 capture by low surface area 10 μm and 20 μm precalcines. Grain-model predictions based on the sorbent properties and reactor conditions are shown.

In order to test this hypothesis, the Albacar and Albagloss precalcines were injected into the ITR at 1300°C while the electrically heated zone of the reactor was maintained at 1000°C. This produced a thermal history allowing the sorbent to "see" fast kinetics at short times as the temperature reached the sulfation window. The results of these tests are shown in Figure 5-5 with time-resolved grain model predictions. The grain model predictions are based upon the measured gas temperature profile.

The grain model does not account for thermal deactivation of the sorbent. However, because of the rapid temperature drop the predicted capture level is much lower than that predicted for 1200°C under isothermal conditions. Nevertheless, and despite a shorter residence time, the measured SO_2 captures (Ca/S = 2.0) for each of these precalcines are higher than those obtained at 1000°C and 1200°C.

5.2 Precalcine Sintering Tests

Surface area measurements were conducted on samples of precalcines extracted from the isothermal reactor at the 1000°C and 1200°C conditions without SO_2 addition. For seven of the precalcine materials, surface area was measured only at the reactor exit (about one second residence time). In addition, time-resolved data were obtained with the 32 m^2/g 10 μm MW 125 precalcine. Limited sampling was also done at the 1300/1000°C condition.

The purpose of these data was: (1) to determine the extent to which the surface area assumption of the model is justified by the data, (2) to lend insight into physical reasons for the form of the sulfation data, and (3) to determine whether small particle size provides resistance to sintering.

Figure 5-6 shows the time-resolved sintering data for the 10 μm precalcine. As expected, the surface area was reduced much further at 1200°C than at 1000°C. The problems of sampling from a reactive gas stream are recognized and addressed in Appendix (C). Potential sampling effects notwithstanding, the difference in surface areas measured at the two

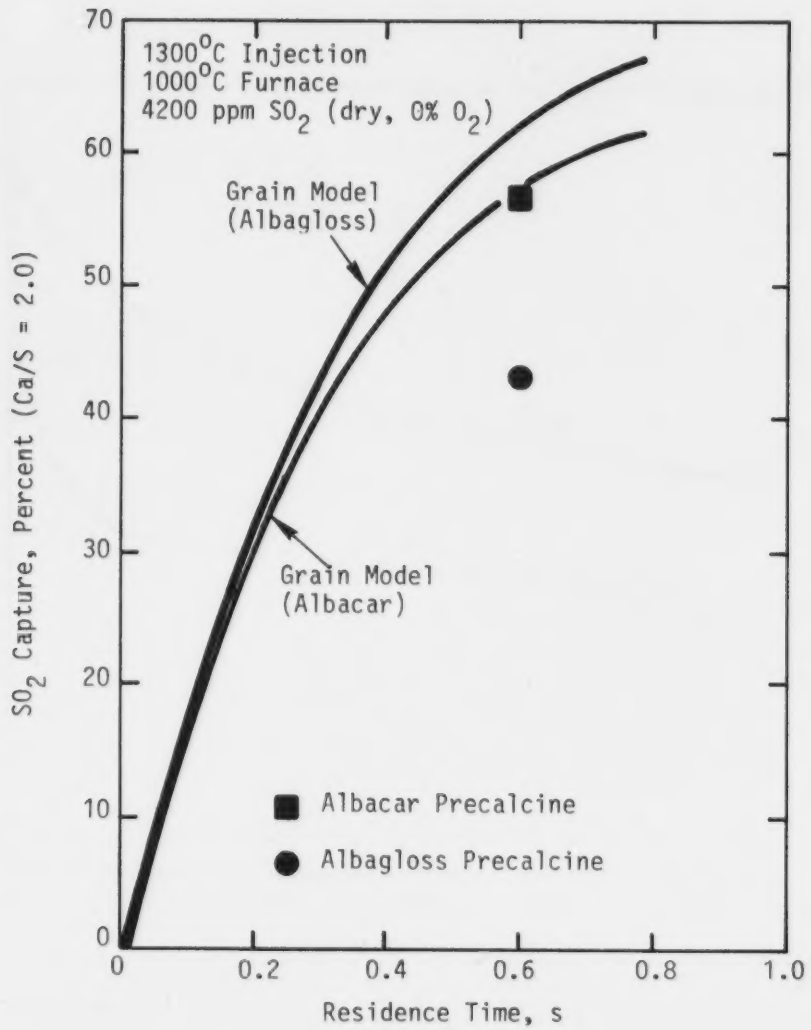

Figure 5-5. Results of high temperature injection tests with Albacar and Albagloss precalcines. Time-resolved grain model predictions are shown with the data.

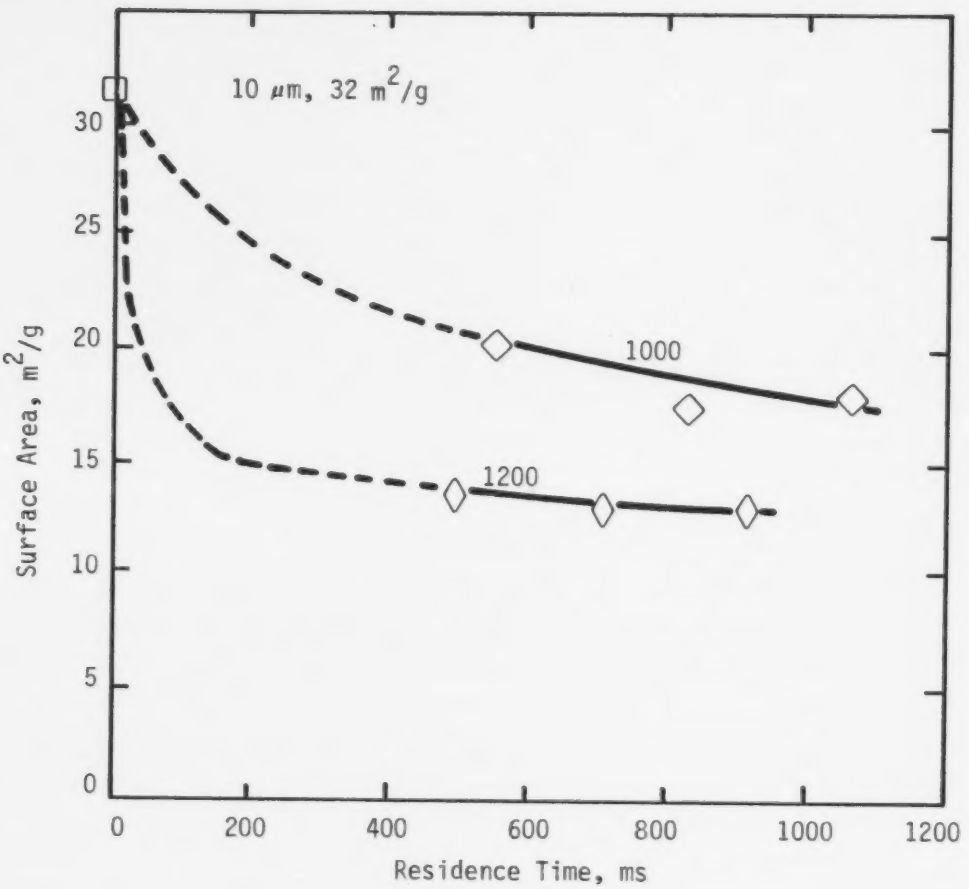

Figure 5-6. Surface area profiles for 10 μm, 32 m^2/g precalcine at 1000°C and 1200°C.

temperatures is significant and demonstrates that the model assumption of constant surface area is inadequate.

The results shown in Figure 5-6 do, however, address the issue of the form of the sulfation data. The shapes and relative magnitudes of the surface area profiles confirm the predictions made in an earlier study (9). In that study, the differences between model predictions and sulfation data were used to numerically deduce the surface area profiles during sulfation. The rapid initial loss of surface area corresponds roughly to the initial uptake of SO_2 shown in Figure 5-1. The subsequent leveling-off of the sulfation rate is believed to result from the lower surface area available after about 250 ms. While the surface areas predicted in the earlier study were lower than those in Figure 5-6, it should be recognized that the presence of calcium sulfate is known to accelerate the rate of sintering (12).

The surface area test results for the other sorbents and operating conditions are shown in Table 5-1. (The supply of Multifex precalcine was exhausted before these tests could be run.) Although the data suggest a slightly lower surface area for the high temperature conditions, no significant impact of particle size is indicated. Since decreasing particle size could improve reactivity through (1) an enhanced CaO surface area, and (2) a reduction in pore diffusion resistance, these data suggest the importance of latter phenomenon relative to the former.

5.3 Hydrate/Carbonate Reactivity Studies

For several years it has been recognized that hydrated limes (calcium hydroxides) as a group, experience higher utilizations within the same environment than limestone, or carbonate, sorbents (7). More recently it was shown that even on the basis of constant initial particle size hydrates achieved higher SO_2 capture than carbonates (6). It has also been well established that under some conditions limestone sorbents will fragment upon injection at high-temperature (5,8). The purpose of this task was to

TABLE 5-1. SURFACE AREAS OF PRECALCINED SORBENTS AFTER INJECTION INTO THE ITR

Sorbent	Specific Surface Area, m^2/g		
	1000°C, 1.07 s	1200°C, 0.92 s	1300/1000°C, 0.6 s
20 μm, 27 m^2/g	20[a]	17[b]	
20 μm, 12.5 m^2/g	10	10	
10 μm, 32 m^2/g	19	12	
10 μm, 11.7 m^2/g	10	11	
EERC Fines, 27 m^2/g	16	13	15
Albacar Precalcine 25 m^2/g	15	11	
Albagloss Precalcine 27 m^2/g	18	13	14

[a] 0.7 s

[b] 0.6 s

determine whether a difference in in-situ particle size could explain the superior hydrate reactivity.

5.3.1 Particle-Size Sulfation Studies

A sorbent reactivity baseline was established using three hydrate and two carbonate sorbents. These were obtained by aerodynamic classification of (respectively) Linwood atmospheric hydrate and Vicron 45-3. Sulfation data for the five sorbents are presented in Figure 5-7.

The sulfation data are shown again in Figure 5-8, this time indicating the correlation between particle size and SO_2 capture (at Ca/S = 2.0). Also indicated in the figure are data obtained in the EER Controlled Temperature Tower (CTT) (6). The ITR data confirm the effect seen on the CTT, but no inference should be made about the relative magnitudes of the two data sets. The CTT data were obtained under non-isothermal conditions and at a much longer residence time.

5.3.2 In-Situ Sorbent Properties

The 8.8 μm carbonate and 9.4 μm hydrate, because of their proximate sizes, were chosen for cascade impactor sampling. The samples were collected at a residence time of 475 ms using the impactor sampling system described in Section 4.1.

The results of the impactor sampling tests are shown in Figure 5-9 for the raw hydrates and Figure 5-10 for the raw carbonate. Two tests were run with each sorbent. These are indicated by the open and closed symbols on the graphs. Also shown are the curves obtained by Sedigraph size analysis on the raw materials.

The agreement between the impactor sizing and the sedigraph is far better than expected. Within the accuracy of the cascade impactor data no change in particle size distribution is evident for either sorbent. This

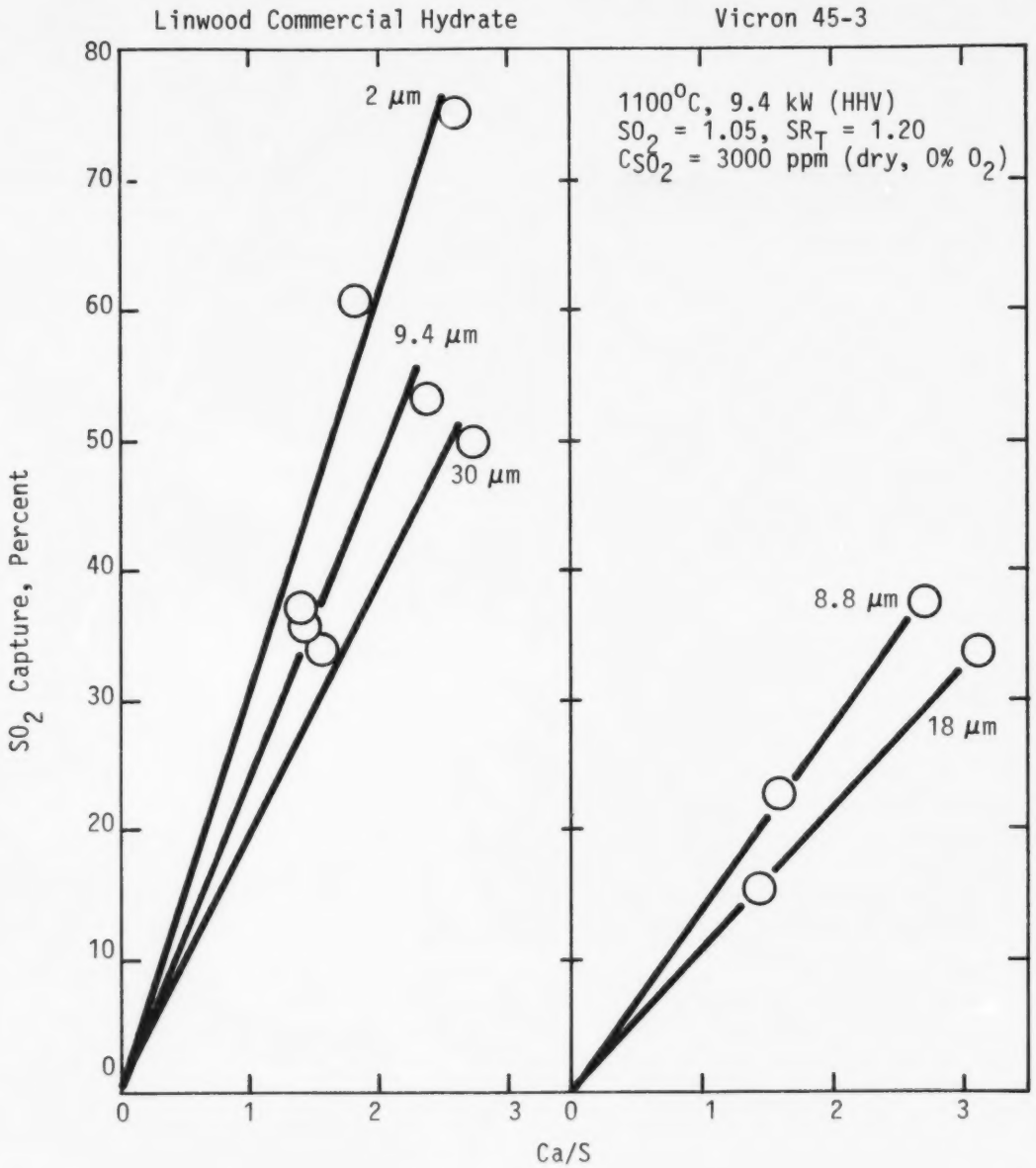

Figure 5-7. Particle size vs. sulfation data for raw, size classified hydrates and limestones.

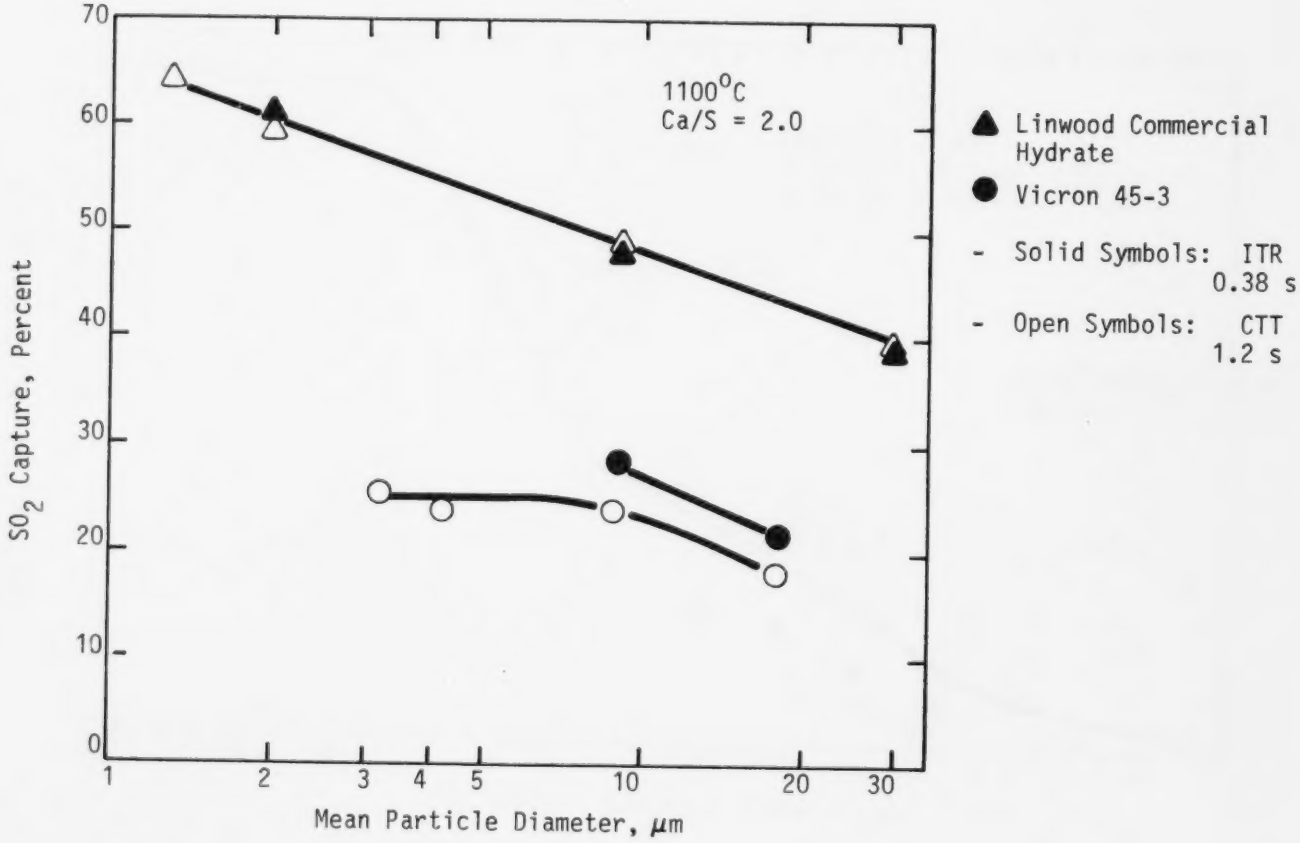

Figure 5-8. Particle size dependence of SO_2 capture by Linwood atmospheric hydrate and Vicron 45-3. The open symbols represent data taken on the Controlled Temperature Tower (6).

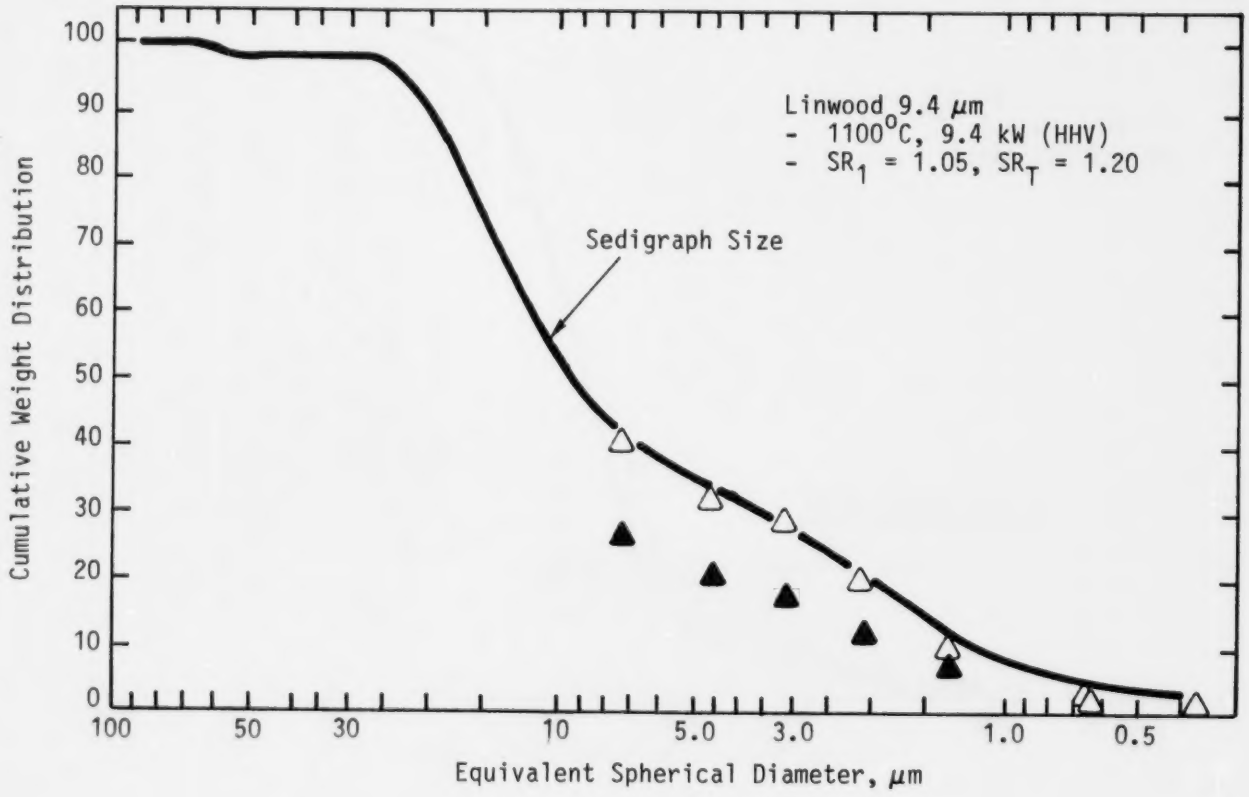

Figure 5-9. Comparison of in-situ particle size for 9.4 μm Linwood hydrate (determined by cascade impactor sampling) with the pre-reactor particle size determined by sedigraph analysis. Open and shaded symbols represent independently repeated runs.

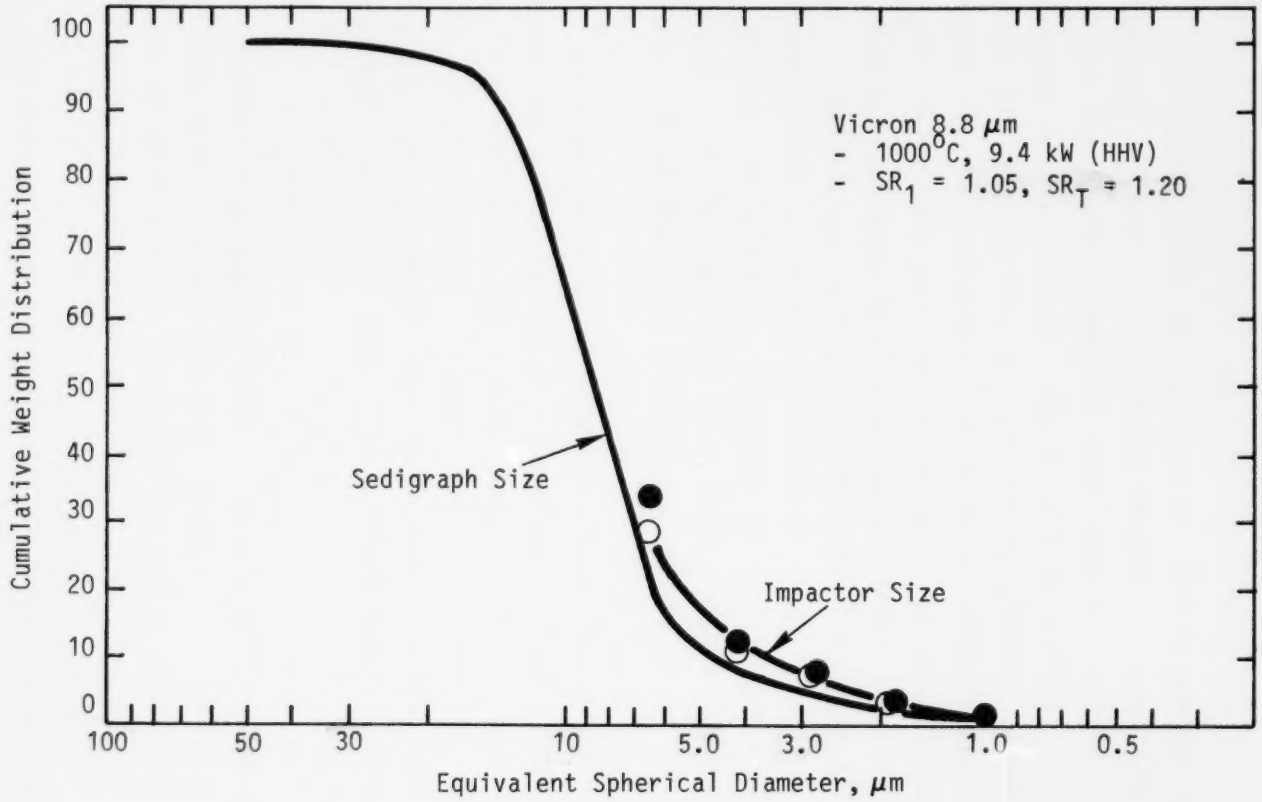

Figure 5-10. Comparison of in-situ particle for 8.8 μm (determined by Cascade impactor sampling) with the pre-reactor particle size determined by sedigraph analysis. Open and closed symbols represent independently repeated runs.

suggests that thermal comminution of the larger hydrate and carbonate particles does not occur under practical injection temperatures.

5.4 Summary

Sulfation tests using size-classified precalcines confirmed the dependence of calcium utilization on particle size. The results suggested that influences beyond particle size, pore structure, or surface area had an influence on utilization. Due to this variability, it was not possible to verify conclusively that the size for pore/product transition was correctly selected by the grain model. At 1200°C the model overpredicted the capture, a point which indicates the necessity of including sintering in the model. In addition, two separate size vs. capture trends were indicated by the data. One for the PCC precalcines and the other for the MW 125 precalcines. Low surface area precalcines were used to study sulfation under reduced pore diffusion resistance. However, as the grain model had suggested (Figure 1-1), the decrease in surface area had only a small impact on the reactivities of the larger diameter precalcines.

The high-temperature injection tests did not provide insight as to whether small particles are more resistant to thermal deactivation. However, the results suggest that higher capture levels might be obtained under quenched rather than isothermal operation. Despite the shorter residence time and rapid quench rate, the capture levels under the 1300/1000°C condition were higher than those achieved isothermally at either 1000°C or 1200°C.

Surface area sampling tests bring into question the model assumption of constant surface area. The data showed both residence time and temperature effects on surface area. The parametric tests, however, showed no impact due to particle size on surface area loss.

The hydrate/carbonate reactivity tests showed that on a common size basis hydrates are more reactive than carbonates. The impactor data demonstrated that thermal comminution of the large-size hydrate fraction does

not occur during exposure to the reactor gas. Thus, the enhanced reactivity of hydrates is not indicated to be due to thermal fragmentation within the reactor.

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APPENDIX A

EXPERIMENTAL DATA

Table A-1. Sulfur Capture Data. Precalcines Studies

Sorbent	Surface Area m^2/g	Temperature °C	Residence Time s	SO2 Capture Percent	Ca/S	Capture @ Ca/S 2.0
20 um	27	1000	0.19	15.5	2.09	
"	"	"	0.19	14.3	2.13	
"	"	"	0.19	11.6	1.70	14.0
"	"	"	0.32	12.9	1.83	14.0
"	"	"	0.44	12.2	1.88	
"	"	"	0.44	14.2	1.94	13.8
"	"	"	0.57	14.2	1.85	15.4
"	"	"	0.69	15.0	1.88	
"	"	"	0.69	14.5	1.71	
"	"	"	0.69	15.3	1.72	16.8
"	"	"	1.07	17.6	1.84	19.2
20 um	27	1200	0.27	16.9	1.54	22.Ø
"	"	"	0.38	14.7	1.11	26.4
"	"	"	0.49	11.4	1.28	17.8
"	"	"	0.71	14.7	1.26	23.4
"	"	"	0.92	16.2	1.32	
"	"	"	0.92	16.2	1.06	
"	"	"	0.92	14.8	1.23	26.2
10 um	32	1000	0.19	13.9	1.75	16.0
"	"	"	0.32	12.9	1.78	14.6
"	"	"	0.44	17.4	1.98	17.6
"	"	"	0.57	17.4	1.81	19.2
"	"	"	0.82	16.7	1.81	
"	"	"	0.82	21.7	2.01	20.0
"	"	"	1.07	27.3	2.61	
"	"	"	1.07	24.5	2.37	
"	"	"	1.07	19.0	1.83	20.8
10 um	32	1200	0.27	13.7	1.18	
"	"	"	0.27	12.1	1.29	
"	"	"	0.27	9.4	1.18	19.2
"	"	"	0.38	15.1	1.34	
"	"	"	0.38	9.6	1.51	17.4
"	"	"	0.49	12.2	1.32	
"	"	"	0.49	10.8	1.37	17.2

Table A-1. Sulfur Capture Data. Precalcines Studies

Sorbent	Surface Area m^2/g	Temperature °C	Residence Time s	SO2 Capture Percent	Ca/S	Capture @ Ca/S 2.0
10 um	32	1200	0.71	10.4	1.36	
"	"	"	0.71	14.7	1.55	17.2
"	"	"	0.92	16.7	1.54	
"	"	"	0.92	13.4	1.55	
"	"	"	0.92	18.4	1.42	
"	"	"	0.92	16.2	1.11	23.0
20 um	12.5	1000	0.32	11.1	1.75	12.6
"	"	"	0.44	9.7	1.73	11.2
"	"	"	0.54	11.8	1.58	15.0
"	"	"	0.69	12.3	1.72	14.4
"	"	"	1.07	18.4	1.70	
"	"	"	1.07	14.3	1.54	20.2
10 um	11.7	1000	0.44	6.1	1.54	8.0
"	"	"	0.54	5.5	1.14	9.6
"	"	"	0.69	9.6	1.31	14.6
"	"	"	1.07	11.0	1.64	13.4
Fines	27	1000	0.32	8.1	0.65	24.8
"	"	"	0.44	23.8	1.49	31.8
"	"	"	0.54	35.4	2.14	33.2
"	"	"	0.82	37.7	1.73	43.6
"	"	"	1.07	42.1	1.79	47.0
Fines	27	1200	0.27	27.0	1.25	43.2
"	"	"	0.38	22.7	1.09	41.6
"	"	"	0.49	32.4	1.49	43.6
"	"	"	0.71	27.0	1.41	38.4
"	"	"	0.92	18.2	0.74	49.4
Albacar	25	1000	0.32	33.1	1.97	33.6
"	"	"	0.57	37.8	1.77	
"	"	"	0.57	31.9	1.41	43.8
"	"	"	1.07	14.1	0.61	46.2
Albacar	25	1200	0.27	35.1	1.94	

Table A-1. Sulfur Capture Data. Precalcines Studies

Sorbent	Surface Area m^2/g	Temperature °C	Residence Time s	SO2 Capture Percent	Ca/S	Capture @ Ca/S 2.0
Albacar	25	1200	0.27	30.1	~~2.85~~ 2.03	32.8
"	"	"	0.38	23.0	1.44	32.0
"	"	"	0.49	30.6	1.63	
"	"	"	0.49	30.1	1.91	34.2
"	"	"	0.71	24.5	1.62	
"	"	"	0.71	31.3	1.90	31.8
"	"	"	0.92	30.1	1.73	
"	"	"	0.92	31.5	1.84	34.6
Albacar	25	1300/1000	0.60	25.7	1.13	
"	"	"	0.60	44.3	1.54	
"	"	"	0.60	45.5	1.41	56.6
Albagloss	27	1000	0.32	6.1	0.66	18.6
"	"	"	0.44	7.4	0.72	20.4
"	"	"	0.57	19.6	2.04	19.2
"	"	"	0.82	11.3	0.96	
"	"	"	0.82	14.0	1.02	
"	"	"	0.82	15.7	1.55	23.2
"	"	"	1.07	16.0	1.15	
"	"	"	1.07	27.5	1.80	
"	"	"	1.07	32.0	2.83	26.2
Albagloss	27	1200	0.27	10.5	1.40	15.0
"	"	"	0.38	17.5	1.48	23.6
"	"	"	0.49	16.9	1.25	27.0
"	"	"	0.60	20.8	1.41	29.6
"	"	"	0.92	18.9	1.11	34.2
Albagloss	27	1300/1000	0.60	15.4	0.97	
"	"	"	0.60	18.8	0.85	
"	"	"	0.60	19.3	0.68	
"	"	"	0.60	19.8	0.90	43.2
Multifex	25	1000	0.19	31.0	1.48	42.0
"	"	"	0.32	35.1	1.77	39.6
"	"	"	0.44	36.5	1.70	43.0

Table A-1. Sulfur Capture Data. Precalcines Studies

Sorbent	Surface Area m^2/g	Temperature °C	Residence Time s	SO2 Capture Percent	Ca/S	Capture @ Ca/S 2.0
Multifex	25	1000	0.57	44.6	1.77	50.2
"	"	"	0.69	30.4	1.24	49.0
"	"	"	1.07	31.0	1.24	50.0
Multifex	25	1200	0.38	26.7	1.47	36.4
"	"	"	0.49	23.0	1.12	
"	"	"	0.49	23.7	1.42	36.8
"	"	"	0.71	26.3	1.22	43.2
"	"	"	0.92	23.1	0.98	
"	"	"	0.92	29.7	1.62	36.6

TABLE A-2. SULFUR CAPTURE DATA--HYDRATE/CARBONATE STUDIES

Sorbent	Size (μm)	Temperature (°C)	Residence Time (s)	SO_2 Capture (%)	Ca/S	Utilization (%)
Linwood	2 μm	1100°C	0.38	60.9	1.82	
Linwood	2 μm	1100°C	0.38	75.3	2.60	30.8
Linwood	9.4 μm	1100°C	0.38	35.7	1.43	
Linwood	9.4 μm	1100°C	0.38	37.2	1.40	
Linwood	9.4 μm	1100°C	0.38	53.3	2.39	24.2
Linwood	30 μm	1100°C	0.38	33.9	1.58	
Linwood	30 μm	1100°C	0.38	49.8	2.75	19.3
Vicron	8.8 μm	1100°C	0.38	22.7	1.58	
Vicron	8.8 μm	1100°C	0.38	37.3	2.72	14.0
Vicron	18 μm	1100°C	0.38	15.5	1.44	
Vicron	18 μm	1100°C	0.38	33.7	3.11	10.8

TABLE A-3. CASCADE IMPACTOR STAGE CUT DIAMETERS

Stage No.	Diameter (μm)							
	Vicron 8.8 μm		Vicron 8.8 μm		Linwood 9.4 μm		Linwood 9.4 μm	
	Test 1		Test 2		Test 3		Test 4	
	$D_{S,50}$	$D_{A,50}$	$D_{S,50}$	$D_{A,50}$	$D_{S,50}$	$D_{A,50}$	$D_{S,50}$	$D_{A,50}$
0	6.5	10.9	6.5	10.8	7.4	11.1	7.2	10.8
1	4.1	6.9	4.1	6.9	4.6	7.0	4.6	6.9
2	2.8	4.7	2.8	4.7	3.2	4.8	3.1	4.7
3	1.9	3.2	1.9	3.2	2.1	3.2	2.1	3.2
4	1.2	2.0	1.2	2.0	1.4	2.1	1.3	2.0
5	0.6	1.0	0.6	1.0	0.7	1.0	0.6	1.0
6	0.3	0.6	0.3	0.6	0.4	0.6	0.4	0.6
7	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4

TABLE A-4. CASCADE IMPACTOR MASS LOADING DATA

Sorbent	Net Mass (mg) on Stage										
	P*	0	1	2	3	4	5	6	7	F**	Total
Vicron, 8.8 µm Test 1	42.4	20.4	15.5	2.9	4.1	2.2	0.6	0.0	-	-	88.1
Vicron, 88.8 µm Test 2	14.6	11.0	8.3	1.7	1.6	0.9	0.4	0.1	-	-	38.6
Linwood, 9.4 µm Test 1	12.1	12.3	3.5	1.5	3.8	4.4	3.0	0.7	0.0	-	41.3
Linwood, 9.4 µm Test 2	27.2	15.3	3.7	1.4	3.7	3.1	3.2	0.4	-	-	58.0

*Test Preseparator

**Filter

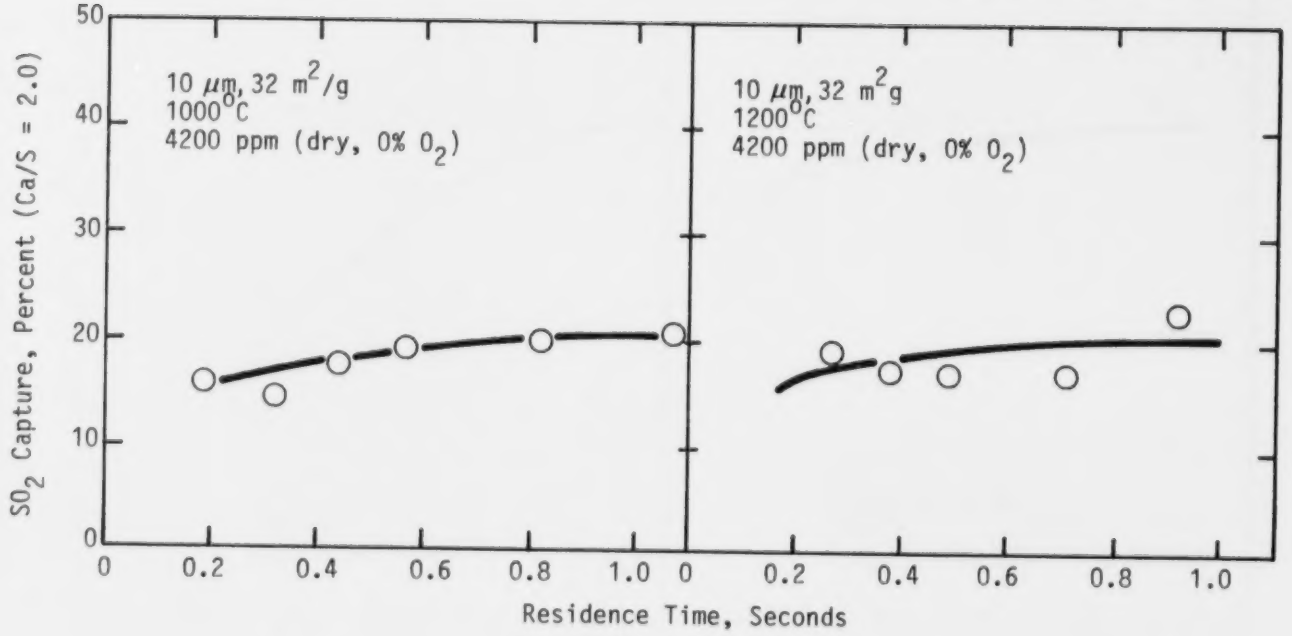

Figure A-1. Time-resolved sulfation for 10 μm, 32 m^2g MW125 precalcine.

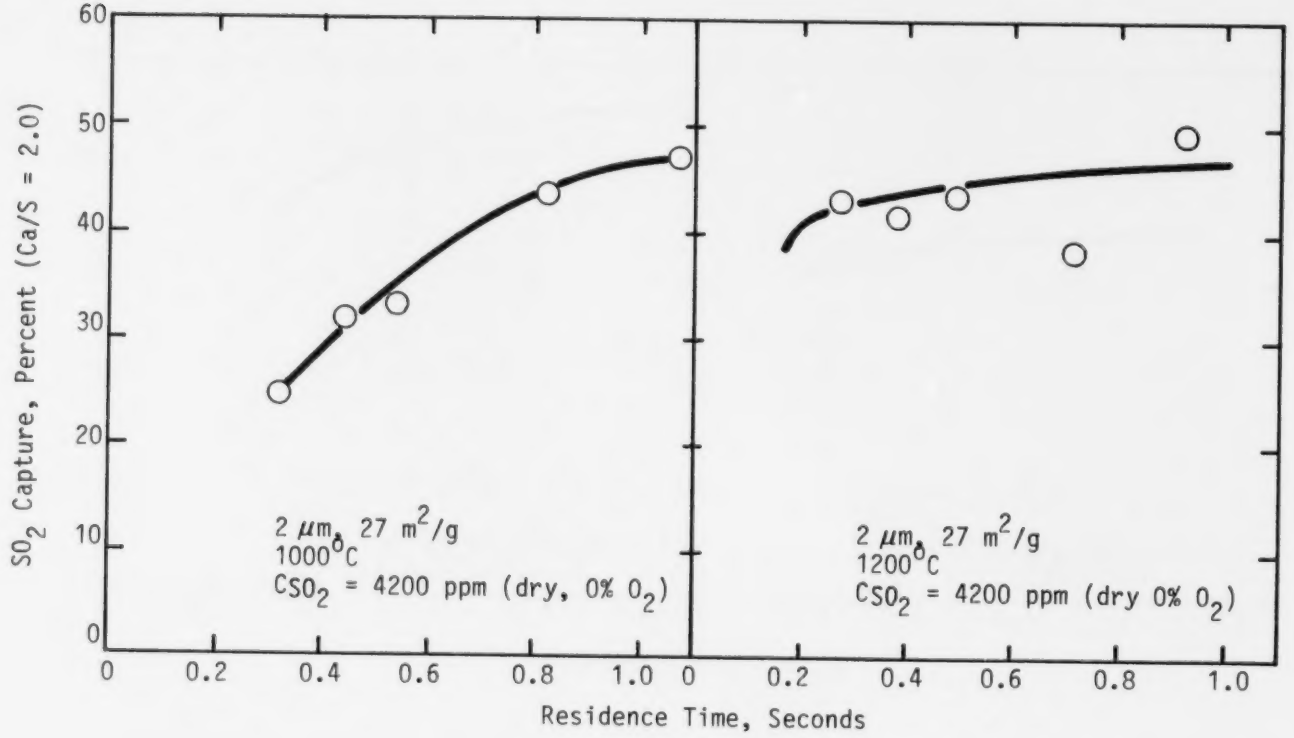

Figure A-2. Time-resolved sulfation data for 2 μm, 27 m^2g MW125 precalcine.

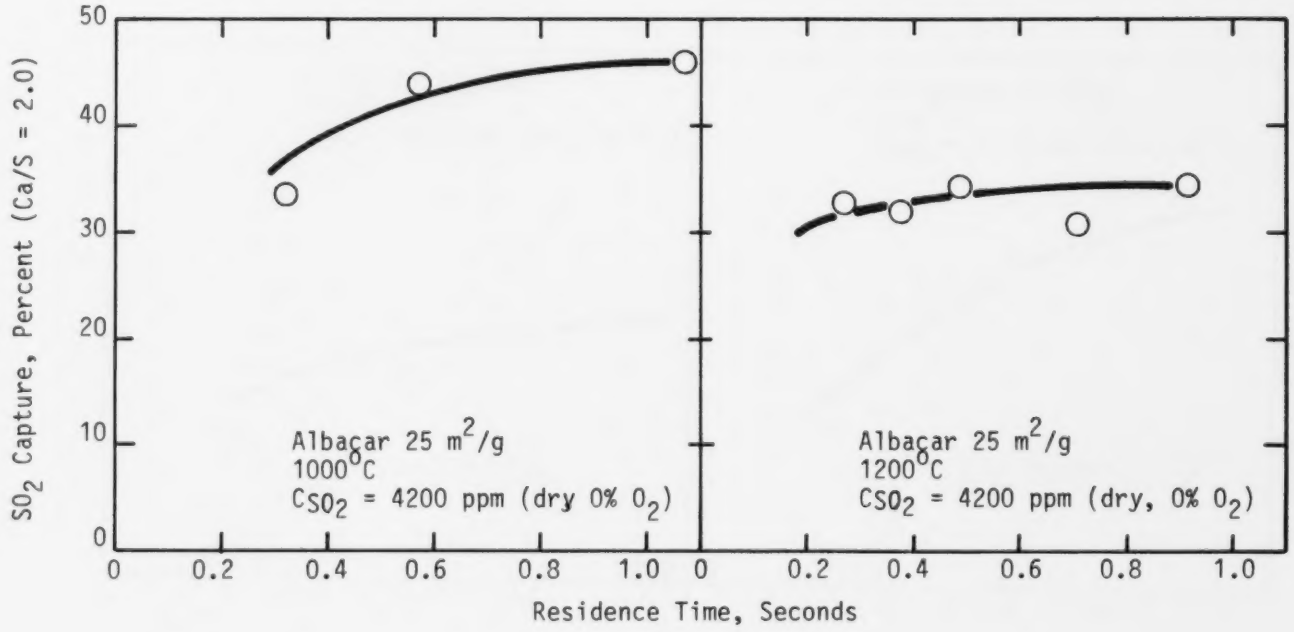

Figure A-3. Time-resolved sulfation data for Albacar 25 m^2/g PCC precalcine.

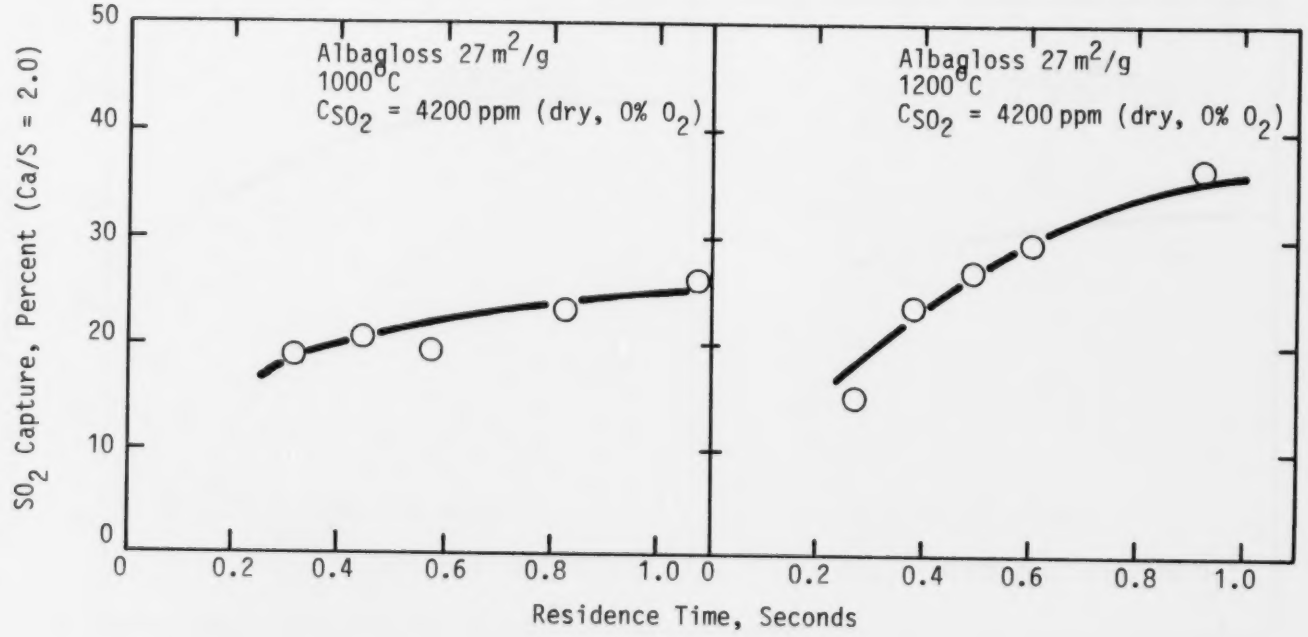

Figure A-4. Time-resolved sulfation data for Albagloss 27 m^2/g PCC precalcine.

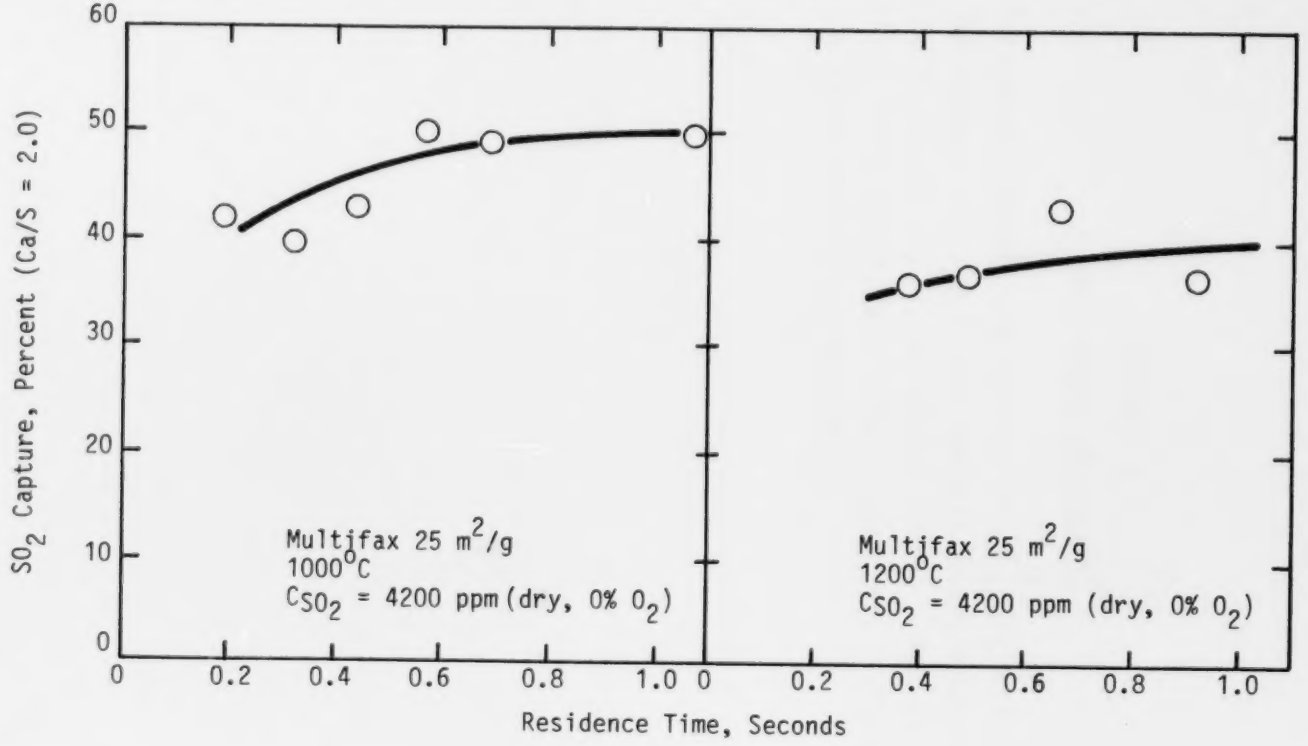

Figure A-5. Time-resolved sulfation data for Multifax 25 m^2/g PCC precalcine.

APPENDIX B

SAMPLE SYSTEM PROCEDURES

The following document is an excerpt from the ITR OPERATIONS MANUAL, an internal EER document which describes the most recent established procedures for operation of the ITR and its peripheral systems. Most of the emphasis in this document is on sampling systems procedures. References are made throughout to other internal EER documents.

ITR OPERATIONS MANUAL

This manual covers the actual operation of the ITR system during experimental testing. It is intended to guide the operator through the process of setting up, collecting data, and proofing to ensure quality, repeatable data.

Several types of tests may be performed in the ITR. These are characterized generally as follows:

1. Gas-phase SO_2 capture measurements
2. Solid sampling (with SO_2) for sulfur balance
3. Solid sample (no SO_2) for (e.g.) surface area
4. Cascade impactor sampling

Each of these tests can be divided into two basic elements: sorbent feeding and sample collection. These tests differ essentially in the sampling elements; however, there are subtle differences in feeding techniques which will be discussed individually. In addition, an appendix is included to serve as a trouble shooting guide. The appendix should be maintained and updated by the operator in charge as, undoubtedly, new situations will constantly arise due to new testing procedures, equipment, or materials.

1) Gas-Phase SO_2 Capture Measurements

Outline -

I. Set up Reactor

II. Set up Gas Phase Sampling System

III. Fire up Reactor

IV. Line Out and Calibrate the SO_2 Analyses and Continuous Monitoring System Analyses

V. Calibrate Sorbent Feeder

VI. Line Out Sorbent Feed System and Reactor

VII. Run Test

VIII. Recalibrate and Line Out Sorbent Feed System

This outline covers the basic steps involved in gas-phase SO_2 capture measurements. Details follow.

I. Set up Reactor

Reactor operating conditions should be determined in advance. These include stoichiometry, firing rate, transport air and sorbent feed rate. Once determined, the reactor should be set up accordingly with the appropriate fuel, air, and transport rotometers on other flow devices. For doping with SO_2 or H_2S (SO_2 is typical) all line connections should be made prior to reactor fire up.

II. Set up Gas-Phase Sampling System

The gas-phase sampling system Figures B-1 and B-2 should be set up prior to starting the burner. This includes all connections between the phase-discrimination probe and the appropriate gas analyzers, as well as installation of the probe into the reactor and adjustment of the probe cooling water flow rate. These preparations are described in the ITR CONTINUOUS MONITORING SYSTEM PROCEDURES manual.

It is important that the system be set up and at temperature before firing the burner to avoid condensation of moisture from the flame gases in the sampling lines.

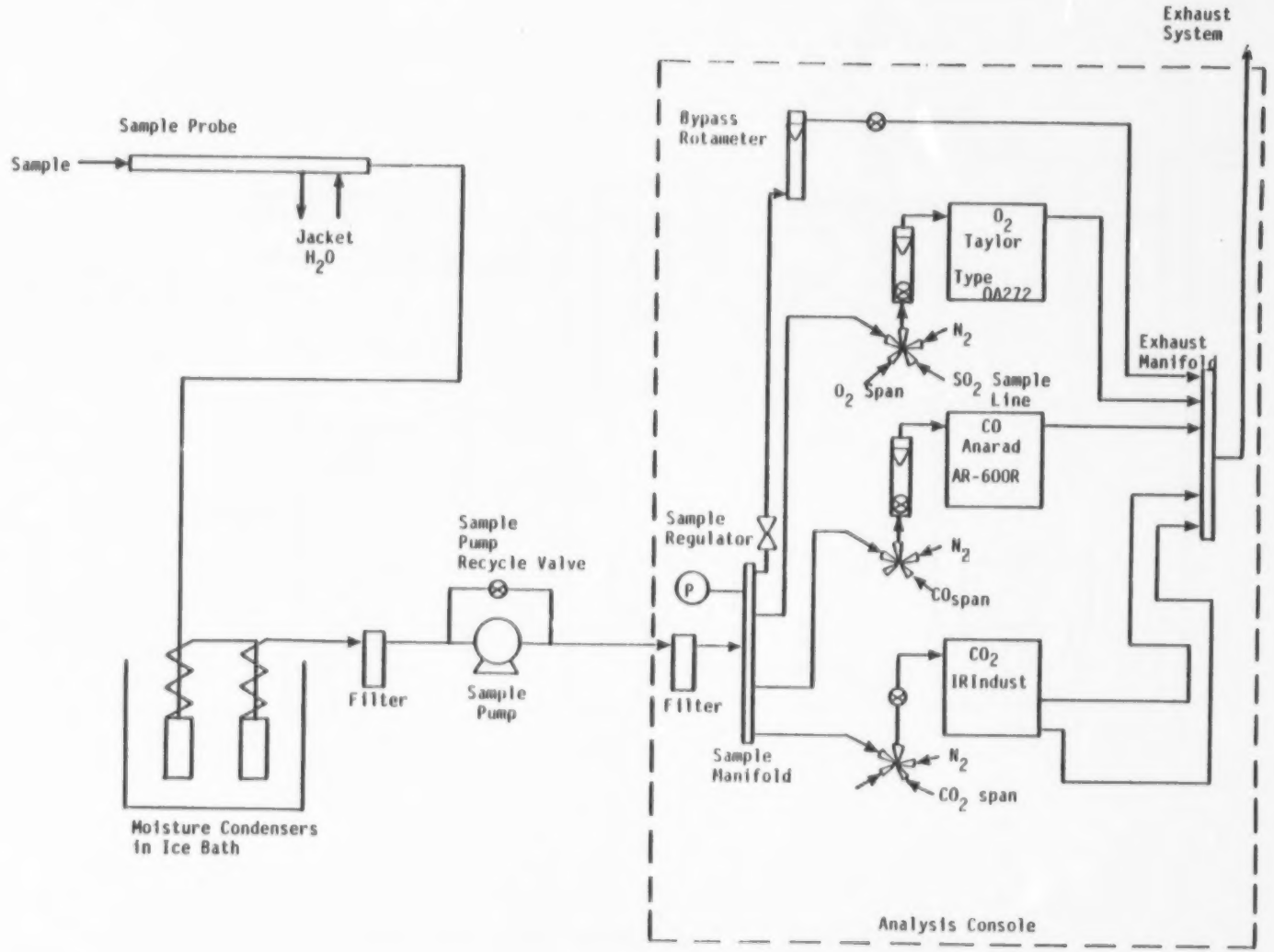

Figure B-1. Continuous monitoring sampling system.

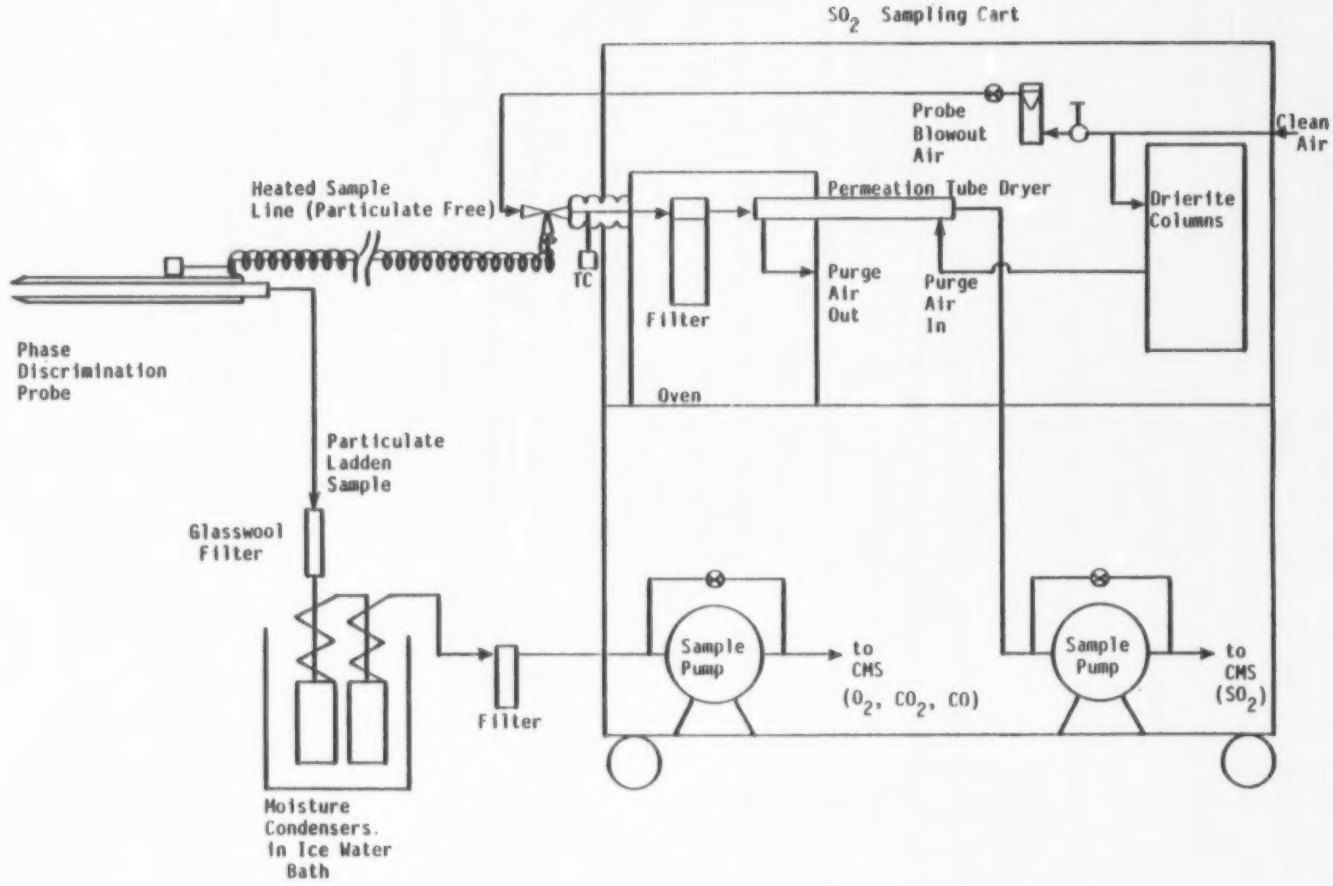

Figure B-2. CMS and SO_2 sampling flow diagram.

III. Fire up Reactor

Light the burner and adjust all gas flow rates in accord with instructions provided in the REACTOR SYSTEM OPERATION manual. Pressure drop across the sintered bronze burner (if used) is a function of total gas flow rate and the temperature of the burner face. As the burner warms up it is normal for the gas flow rates to require readjustment.

IV. Line Out and Calibrate the SO_2 Analyzer and Continuous Monitoring System Analyzer

Calibration of the DuPont (or other) SO_2 analyzer and the CMS analyzers should be done in accordance with the ITR CONTINUOUS MONITORING SYSTEM PROCEDURES MANUAL. It is critical that all flow rates, pressures, and temperatures of the instrument span gases be the same as those measured during sampling. It is a good idea to check them against the sample parameters before beginning the calibration. These parameters also should be checked before and during every test run.

V. Calibrate Sorbent Feeder

The sorbent feeder should be calibrated before and after each test. In this way any change in feed rate during a test can be detected. Assuming an acceptable level of repeatability the feedrate assigned to a test should be an average of the before and after calibrations.

Before that point, however, the feeder should be lined out to constant rate of delivery. When sorbent has just been added to the feeder, this may require 15 to 30 min. Measurements should be made every few minutes until an acceptable level of repeatability at the desired rate is achieved. When merely changing feed rate, as little as 5 min may be sufficient.

Normally, a feed rate is acceptably repeatable if two consecutive measurements are within 10 percent of their mean.

VI. Line Out Sorbent Feed System and Reactor

It is critical that the sorbent feed system and reactor be lined out before each test. This is because all of the components of the sorbent transport system and the sorbent injection (e.g., polyflo tubing, sorbent injector) accumulate some sorbent during a test. The amount of sorbent accumulated may depend on obvious variables, such as sorbent type and feed rate. But, it also may vary according to the operating conditions and the nature of the transport gas. The sorbent injector commonly used (four-port with 3/8" o.d. entrance, water-cooled) has been known to collect over two grams of sorbent while still feeding properly.

A 3-minute lineout is usually sufficient for the feed system to reach steady state. Therefore, after calibrating the feeder, but before the actual test, sorbent should be fed into the reactor for about 3 minutes. If any sort of volumetric feeder (e.g. screw feeder) is used along with an eductor, or other entrainment device, it is necessary to keep the outlet of the feeder at atmospheric pressure. This serves two purposes: 1) it will prevent air from being lost (positive pressure) or entrained (negative pressure) thereby maintaining an O_2 mass balance; 2) it will keep air from moving across the screw into/from the sorbent hopper, which might otherwise alter the sorbent feedrate. A bypass on the transport line leading to the suction side of the eductor may be useful for keeping the pressure at atmospheric. If the eductor starts to plug due to sorbent adhering to its walls, less bypass air will be needed. Therefore, it is necessary to monitor and adjust the bypass constantly while feeding sorbent. A sudden change in the bypass may also affect the transport air flow rate at the source (main flow panel) which therefore must also be monitored.

At the end of the line-out period the reactor walls may be coated with a dusting of sorbent. Also, some sorbent may have been drawn into the sampling probe. It is a good idea at this time to clean the reactor walls with compressed air and to blow the probe clean.

After lineout and cleaning of the reactor walls, the temperature profile (radial) in the precombustor must be checked. This is as much a diagnostic as a means of verifying the sorbent injection temperature. A badly skewed temperature profile may indicate damage to the flow straightener or clogging of an injection port. Also, this is the last opportunity to check the temperature before running the test. See the troubleshooting appendix for explanation of abnormal temperature profiles. Details for setting up and measuring temperature in the isothermal reactor are found in the manual ISOTHERMAL REACTOR: PROCEDURES OF TEMPERATURE CONTROL.

VII. Run Test

After procedures I-VI have been completed the CMS and SO_2 analyzers should be switched to the "Sample" position. The O_2 and SO_2 readings should be monitored on a chart recorder. At this point the O_2 and SO_2 concentrations should also be noted and logged. While these values may change slightly according to probe location, the operator should by now be familiar with limits of error to be expected. (In any case, the probe should be situated as near as possible to the center of the reactor.) If either the SO_2 or the O_2 lie outside of expected limits, see the appendix on troubleshooting.

Once the baseline O_2 and SO_2 have been attained, start the test. It is a good idea to mark, on the chart recorder, the points at which the sorbent feeder is turned on and off. The typical test duration is about 5 minutes.

At the end of the test quickly adjust the transport air flow rate--it has a tendency to drift during sorbent feeding. Allow the SO_2 trace on the chart recorder to continue until the quality of the SO_2 recovery is clear.

VIII. Recalibrate and Line Out Sorbent Feed System

At the end of a test, the sorbent feeder should be recalibrated to determine whether the feed rate has changed. The feed rate assigned to the run (for determining Ca/S ratio) should be an average of the before and after

calibrations. If the next test involves the same feed rate with the same sorbent, then lining out the feed system is probably not necessary. However, if the feedrate is changed, or a new sorbent is used, all of the procedures starting with step IV must be repeated.

2) Solid Sampling (with SO_2) for Sulfur Balance

Outline -

I. Set up Reactor

II. Set up Solids Sampling System

III. Fire up Reactor

IV. Calibrate Sorbent Feeder

V. Line Out Sorbent Feed System and Reactor

VI. Run Test

VII. Collect Sample and Transfer to Storage

I. Set up Reactor

Follow the procedure outlined in Section 1).

II. Set up Solids Sampling System

The solids sampling system is considerably simpler than the gas-phase sampling system but utilizes many common components. These include

- Sample gas and cooling water temperature monitoring
- Water knock-outs
- Sample line filter (Balston Filter)
- High volume rotary vane pump

(Unlike the phase-discrimination probe used for gas sampling, the solids probe is designed to operate isokinetically). When setting up the solids sampling system, a new sample collection filter should be installed in the holder at the base of the probe. This will help to keep the holder clear but will be discarded before testing begins.

III. Fire up Reactor

Follow the procedure outlined in section 1) with the following note: normally while collecting samples for surface area, particle size, or porisimetry analyses no SO_2 is used.

IV. Calibrate Sorbent Feeder

Follow the procedure outlined in section 1).

V. Line Out Sorbent Feed System and Reactor

Follow the procedure outlined in section 1).

VI. Run Test

After procedures I - V have been completed it is time to run the test. Before turning on the sorbent feeder, several operations parameters need to be checked and noted:

i. Check the cooling water exit temperature and the sample temperature. The sample temperature should be approximately 130-180°C. Adjust the cooling water accordingly. Be sure, however, that the cooling water temperature does not fall below the dew point of the sample stream and does not exceed 95°C.

ii. Check the filter holder to be sure that it is dry and clean. Compressed air may be used to blow out any moisture or solid material. Replace the filter with a fresh one.

iii. Check the sampling flow rate and note it.

Turn on the sorbent feeder and allow it to run for the allotted test duration (usually 5 min). During the test one person should be monitoring the sorbent feed system to ensure that everything is operating correctly. At the same time, a second person should monitor the sampling system. All of the above-mentioned parameters should be checked and adjusted periodically. Furthermore, the visual quality of the sorbent feed into the reactor should be carefully monitored. Any explosive bursting or slugging of sorbent through the feed system may contaminate the sample with unreacted sorbent.

Note; a sudden drop in the sampling flow rate usually indicates condensation in the filter holder. In this case the test should be terminated, and the cause of the condensation corrected before resuming testing.

VII. Collect Sample and Transfer to Storage

At the end of the test turn off the sorbent feeder but leave the sampling system running. Carefully but quickly disassemble the filter holder and remove the filter and sample to a petri dish. Next, carefully recover the sample into a tared vial. Log the sample weight in a notebook. Place the vial into a vacuum dessicater (if available) and put under vacuum for at least 5 min. This may help to devolve any adsorbed moisture. Finally, backfill the dessicater with dry nitrogen. Be sure the vial is securely capped before placing it in storage prior to transfer to the analytical lab for analysis.

3) Solid Sampling (Without SO_2) for (e.g.) Surface Area

These procedures are essentially the same as those in section 2) with special regard to the note in 2)-III. If the sample is for SEM analysis, Step V (lining out the sorbent feed system and reactor) must be modified. Instead:

- Carefully remove injection from the precombustor.
- Line out the feed system, including injector, into an exhaust duct.
- Carefully replace the injector.
- Change the filter in the holder and blow the probe clear of particulate matter with compressed air.

4) Cascade Impactor Sampling

Outline -

I. Set up Reactor
II. Set up Impactor and Sampling System
III. Fire up Reactor and Line Out Sorbent Feeder
IV. Warm up Impactor
V. Turn on Impactor Sampling System
VI. Feed Sorbent
VII. Shut Down Sampling System
VIII. Disassemble Impactor

I. Set up Reactor

Reactor operating conditions should be established according to the tests to be run. This includes flame stoichiometry, temperature, and SO_2 level, if necessary.

II. Set up Impactor and Sampling System

Assemble the impactor with preweighed collection substrates (prepared by the analytical laboratory) and a preconditioned backup filter. Do not yet install the impactor.

The impactor sampling system should be assembled according to the diagram in Figure B-3. Cooling water to the sampling probe must be established before the probe is inserted into the reactor. Turn on the oven and preheat it to approx. 100°C. The top of the preseparation may be attached to the base of the probe and left in the oven during warmup.

Turn on the dilution air to the probe. The proper amount of dilution air (or nitrogen) is that which will provide for isokinetic sampling from the reactor with a total sampling rate of 1 acfm (470 N-cm^3/S).

Do not yet install the impactor.

III. Fire up Reactor and Line Out Sorbent Feeder

The reactor should be fired up (if not already done) according to the startup sequence outlined in the REACTOR SYSTEM OPERATION manual. The sorbent feeder also should be lined out (if necessary for the type of feeder being used). Do not line out sorbent into the reactor. Instead, disconnect the transport line at the injector and line out the feeder into the exhaust duct.

IV. Warm up Impactor

Do not further disturb the reactor. Place the assembled impactor into the oven and connect it to the base of the dilution probe. Connect all thermocouple and pressure lines, as well as the sampling line.

- Do Not turn on the sampling pump.

Turn on and adjust the dilution air to the desired setting. Monitor the impactor temperature. If the oven is preheated, the warm up time should not be longer than 30 min. A temperature near 100°C (212°F) is desirable.

V. Turn on Impactor Sampling System

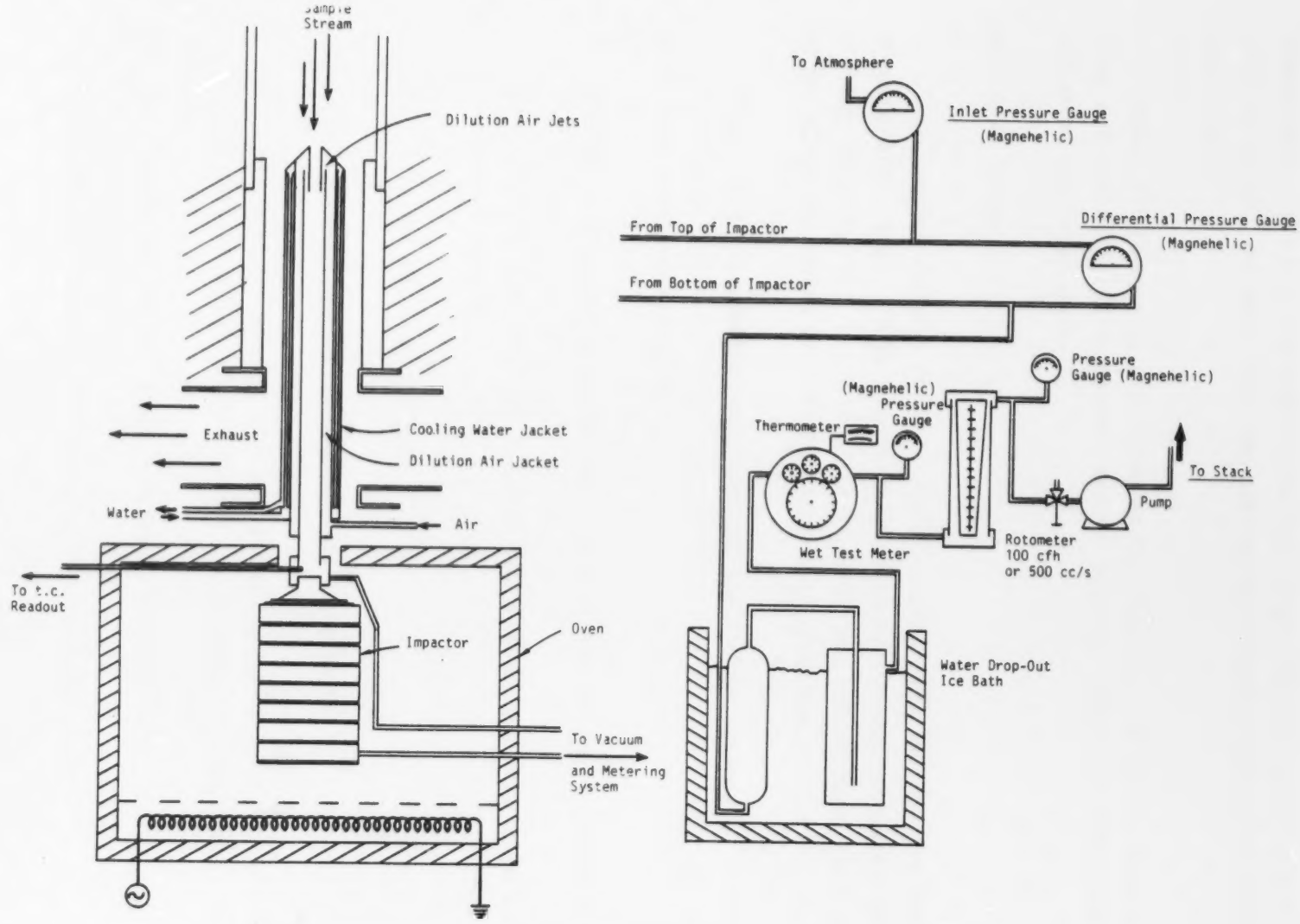

Figure B-3. Schematic of the cascade impactor sampling system for the ITR.

Turn on the impactor sampling pump. Check the impactor sampling temperature. If it is too high or too low, compensate by adjusting the probe cooling water. Be sure that the cooling water outlet temperature does not exceed 90°C.

Adjust all flow rates pertaining to the impactor. Allow the impactor to line out for at least 5 minutes before testing. Check all flow rates and variables and record them.

VI. Feed Sorbent

Turn on the sorbent feeder. Feed sorbent into the reactor for the predetermined time. This time should be based on the estimated solids loading, sampling rate, predicted size distribution, and an upper limit of 10 mg per stage (excluding the preseparator) in the impactor.

After the predetermined time, turn off the sorbent feeder.

VII. Shut Down Sampling System

The impactor sampling system should be shut down in the following order:

1. Turn down sampling rate to below the dilution gas flow rate for at least 5 minutes.

2. Turn off the sampling pump.

3. Disconnect all tubing connected to the impactor.

4. Carefully disengage the nut attaching the impactor to the probe. Be careful not to disturb either the probe or the impactor.

5. Remove the support block from under the impactor.

6. Lower the impactor and remove it from the oven.

During this sequence, it is important that the dilution air be left on. This will prevent any particulate matter in the reactor or near the probe tip from entering the probe. Also, never turn off the dilution air while the sampling pump is operating. The resulting influx of hot reactor gases can overheat and damage the impactor.

VIII. Disassemble the Impactor

The impactor should be allowed to cool to room temperature to facilitate handling. If possible, cover the impactor inlet to prevent contamination by dust or moisture.

Carefully remove the preseparator and transfer the contents to a petri dish, properly labelled and identified. Use a fine camels-hair brush to remove any particulate matter adhering to the metal surface.

One at a time, remove the stage plates and the substrate supports. Remove the substrates carefully and place them in petri dishes. By convention, any material adhering to the stage plate above a given substrate belongs to that substrate. Carefully brush all of the material on the stage plate onto the greased portion of the substrate.

Finally, remove the O-ring holding the backup filter in place and gently remove the backup filter. Be careful not to crease the filter as this may cause some of the glass fibers to be lost, resulting in erroneous weight loss.

When all of the stages and the backup filter have been recovered, place them in a dessicator and transfer them to the lab for drying and weighing.

APPENDIX C

SAMPLING SYSTEM VERIFICATION

APPENDIX C

SAMPLING SYSTEM VERIFICATION

I. Surface Area Sampling

Before attempting to collect solid samples from the ITR for surface area analysis, it was necessary to affirm that the results would not be affected by the sampling procedure. The tests which were performed involved collecting surface area samples at a fixed position in the reactor while varying the sampling conditions. The first and most obvious variable was the temperature at the filter during solids collection. Also examined was the effect of a nitrogen purge at the end of each sample collection period.

The sampling temperature was obtained by means of a 0.5 mm diameter stainless steel sheathed type-K thermocouple placed in the sample stream about 1 cm above the sample filter. The sample temperature was controlled by varying the water flow to the lower cooling jacket of the sampling probe. Temperatures tended to drift (generally downward) during sampling, especially with lower sampling temperatures, and so the range of temperatures is recorded.

Results of sampling temperature tests are shown in Figure C-1. The sorbent used was a 20 micron, 27 m^2/g precalcine. Two ITR temperatures, 1000°C and 1200°C were employed. Although the effects of ITR temperature are apparent, the sampling temperature had only a minor impact.

A nitrogen purge at the end of sampling was employed to sweep away any adsorbed H_2O (or CO_2) which might degrade the sample during storage prior to analysis. The procedure followed was to introduce nitrogen about 2 cm above the sample filter (1 cm above the thermocouple) at a flowrate twice that of the sample flow. This prevented any additional sample from being drawn into the probe; the excess nitrogen being discharged through the top of the probe.

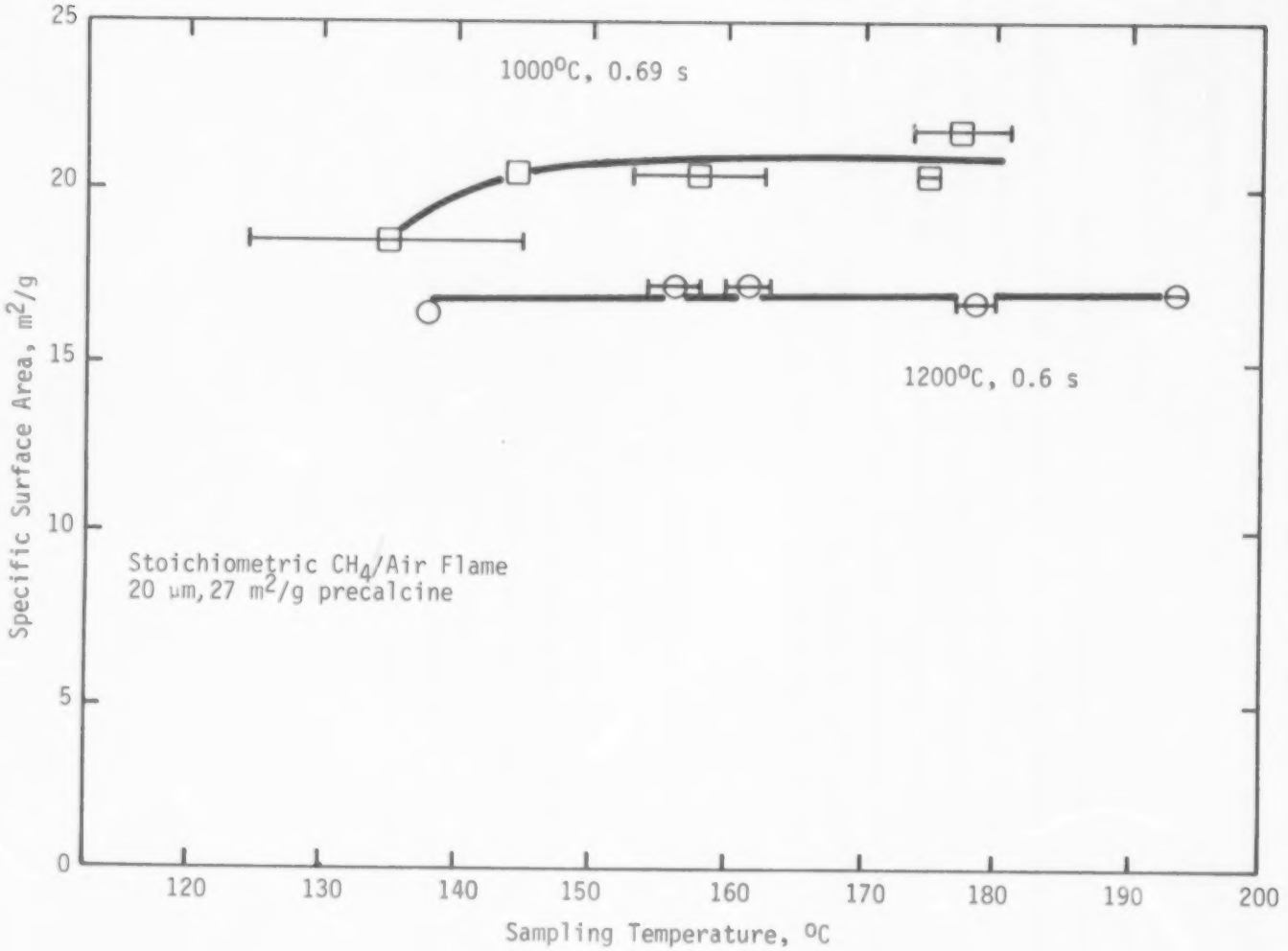

Figure C-1. Effects of sampling temperature on measured specific surface area after furnace injection of a 20 um, 27 m^2/g precalcine.

Results shown in Figure C-2 indicate no effect of nitrogen purge on the measured surface area of the samples over a wide range of sampling temperatures. This test reaffirms the conclusion that sampling temperature (within the observed range) does not affect the measured specific surface area of CaO samples.

II. Sulfur Balance

A "sulfur balance" is basically an agreement between sorbent utilizations calculated from gas-phase data and measured sorbent utilizations obtained from solid samples. Obtaining a sulfur balance in the isothermal reactor served as a means of ensuring that the gas-phase data were not biased by any unknown variable. One particular bias of concern could result if, for example, a significant portion of the sorbent were striking and adhering to the reactor walls. This could increase the apparent utilization determined by gas-phase measurements by effectively increasing the sorbent residence time.

The sulfur balance test was performed under contract EPA 68-02-3987 using a commercial calcium carbonate sorbent Vicron 45-3. The test conditions were the same as those employed for the precalcines' sulfation studies, namely, a stoichiometric CH_4 air flame with 3100 ppm SO_2. Results of these tests are shown in Figure C-3. The shaded symbols in the figure indicate the results from solid sampling. These results indicate that the gas-phase data are correct within the limits indicated by the spread in the data. The sulfur balances (relative to the solid samples results) are:

i $93 \pm 19\%$ at 0.69 s

ii $103 \pm 11\%$ at 1.07 s

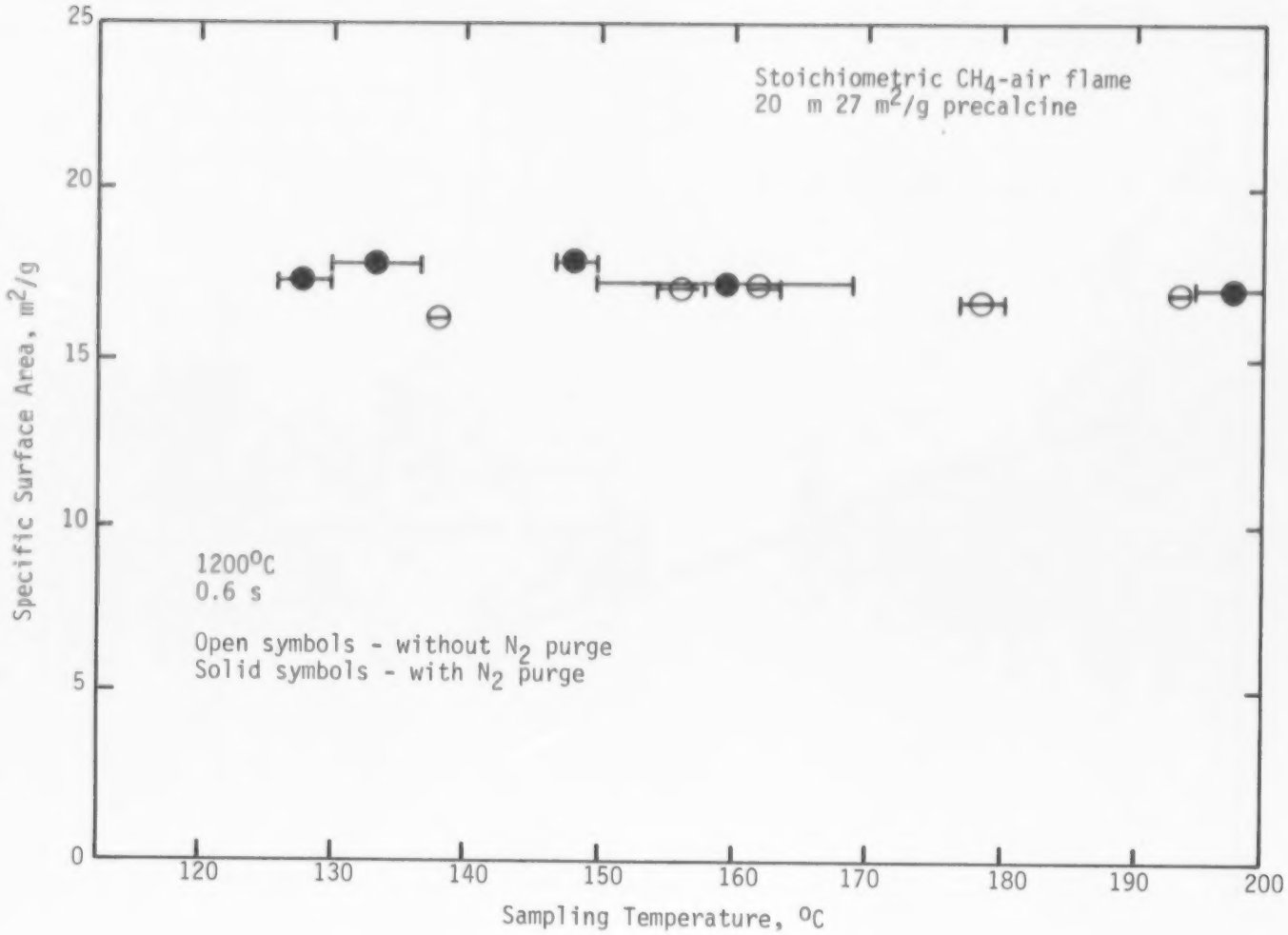

Figure C-2. Effect of N_2 purge after sampling on the measured specific surface areas of samples collected from a 1200°C stoichiometric CH_4-air flame; 0.6 s isothermal residence time.

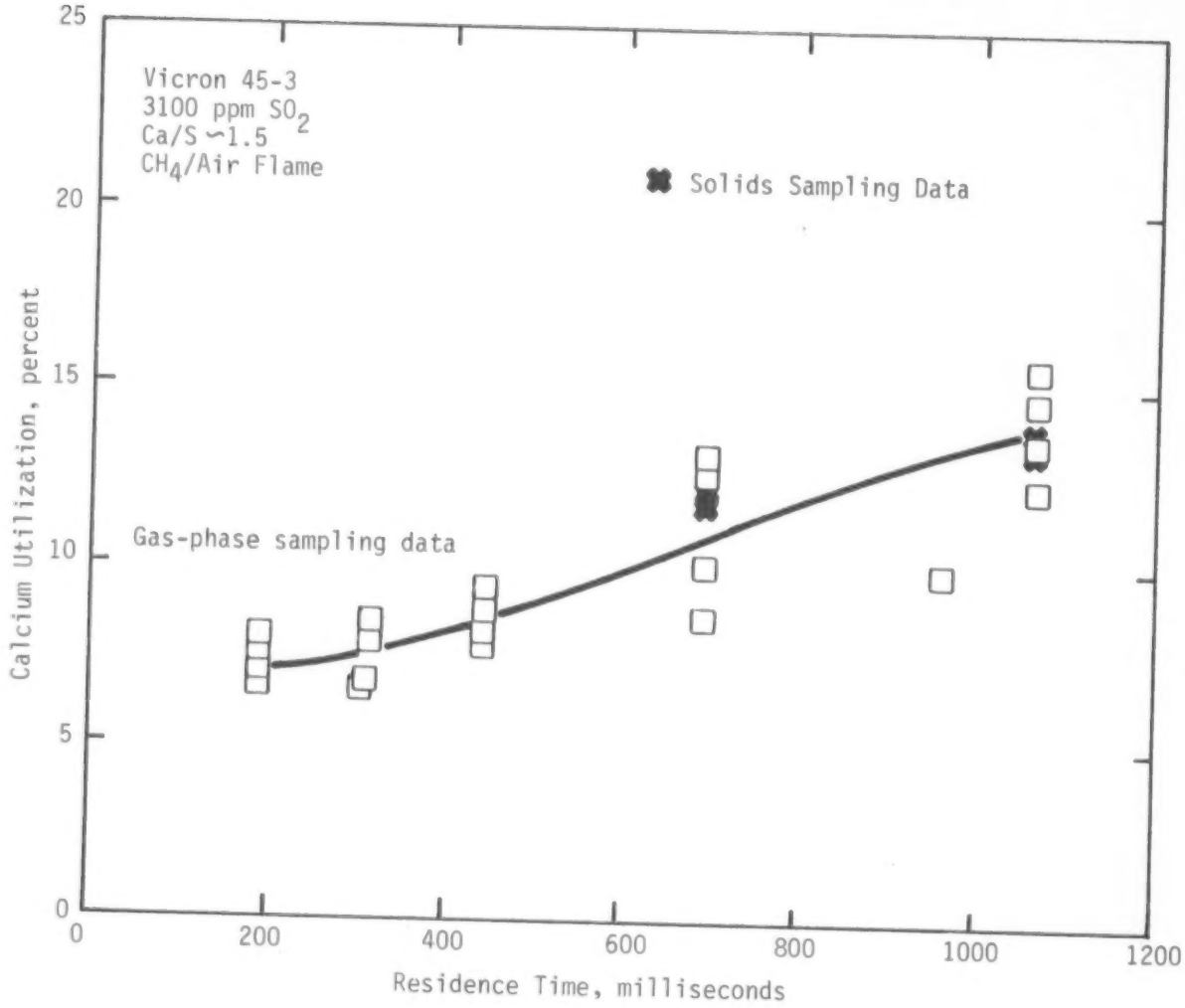

Figure C-3. Comparison of gas-phase data with solid sample analysis to provide a sulfur balance in the ITR.

APPENDIX D

PARTICLE SIZE ANALYSIS

APPENDIX D
PARTICLE SIZE ANALYSES

Particle size distributions for two limestones having mass mean diameters of 21 micron and 10 micron, respectively, are provided in Figures D-1 and D-2. These materials were aerodynamically classified from Marblewhite 125, a commercial limestone. Different size classification techniques were used for the other four starting materials. The EERC fines, also cut from Marblewhite 125, were sized based on SEM examination by the EPA at RTP, NC where the classification was done. The SEM examination indicated a characteristic size of 2-4 microns.

Sizing of the precipitated calcium carbonates was based upon sales literature provided by the supplier, Pfizer Minerals and Pigments Division. The cited sizes were backed up by Pfizer-supplied STEMs as well as a sedigraph analysis for the Albacar 5970. A summary of particle sizes is shown in Table D-1.

After calcination, the sizes of all of the materials were checked by sedigraph analysis. The sizing of porous materials by X-ray sedimentation is subject to some uncertainty due to the possibility of pore filling by the sedimentation medium. This follows from the relation which determines the particle diameter, namely

$$D = k\ (\rho - \rho_f)^{-1/2} \qquad \text{D-1}$$

where:

- D = diameter
- k = a constant, incorporating fluid properties and the terminal velocity of the particle.
- ρ = apparent density of the particle
- ρ_f = density of the fluid

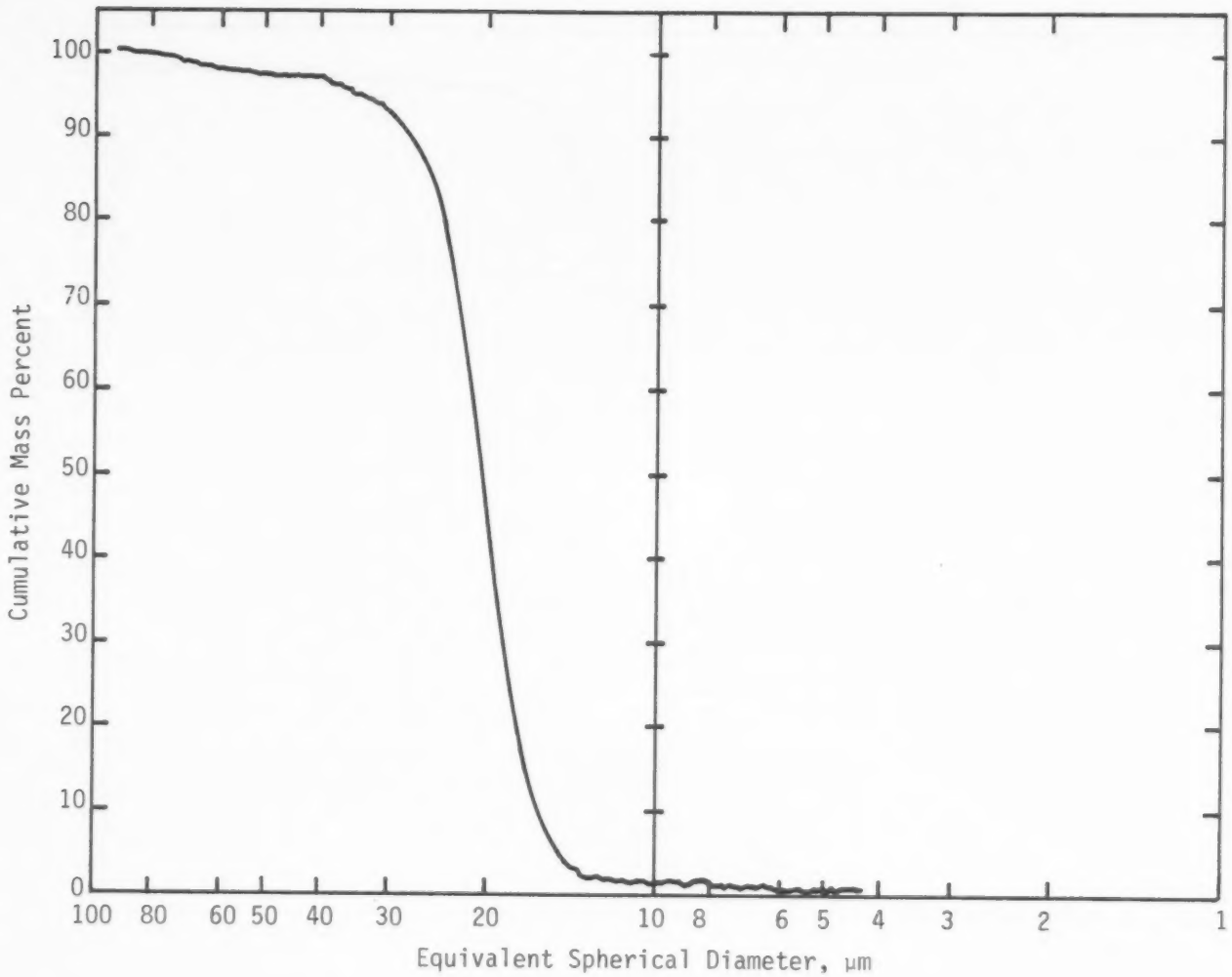

Figure D-1. Sedigraph particle size distribution for aerodynamically classified limestone; 21 μm mass mean diameter.

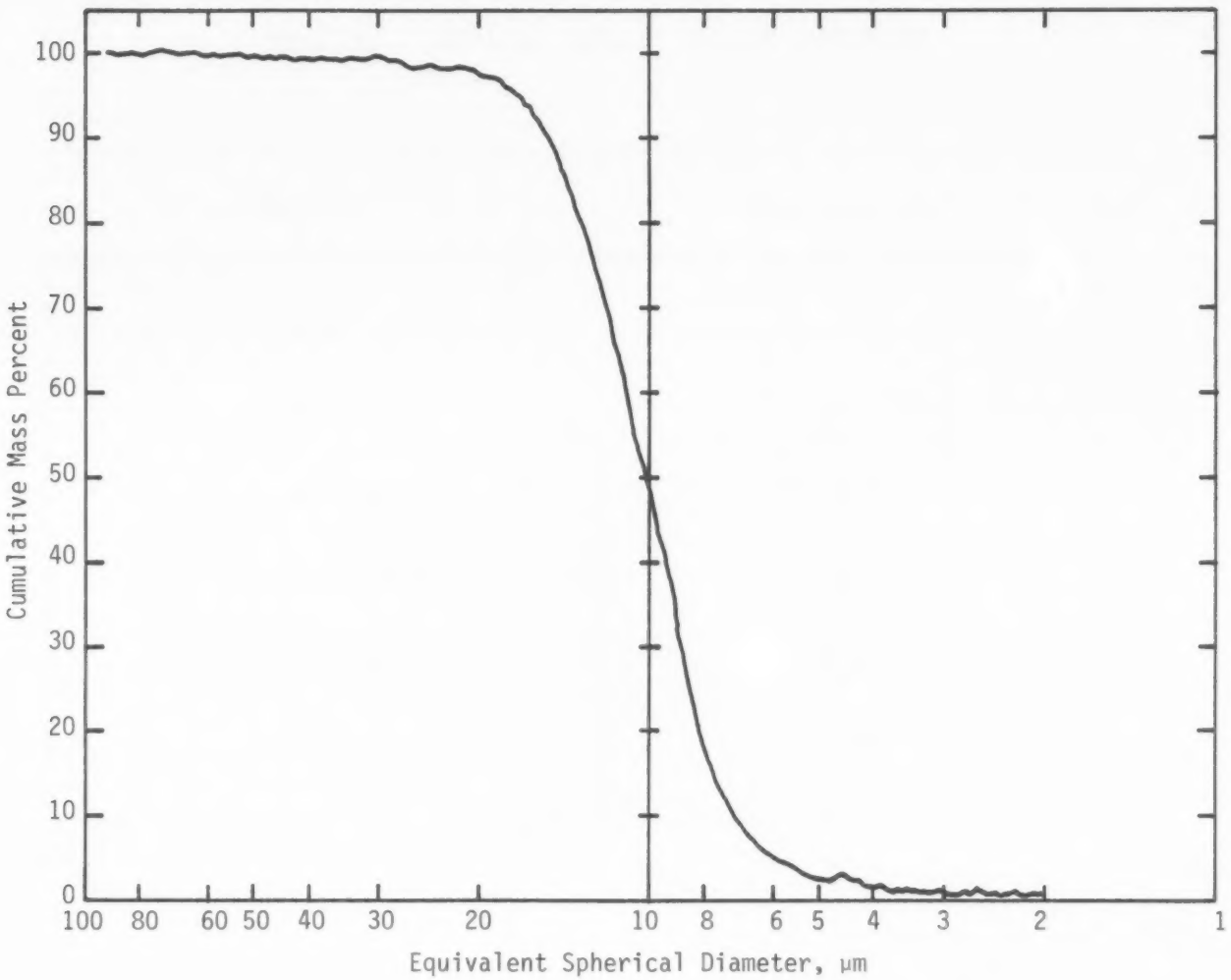

Figure D-2. Sedigraph particle size distribution for aerodynamically classified limestone; 10 µm mass mean diameter.

TABLE D-1. PARTICLE SIZES OF CALCIUM CARBONATES

Material	Mean Size, μm
10 μm	10
20 μm	21
EERC Fines	2
Albacar 5970	2
Albagloss	0.8
Multifex MM	0.07

For a porous material the apparent density is a function of the skeletal density, the porosity, and the density of the fluid occupying the pores. If that fluid is merely air, then it can be ignored. However, if the pores are filled with a liquid material, then that has to be taken into account. Uncertainty is encountered because it is not known whether pore filling occurs, or to what degree it occurs.

Figure D-3 provides the particle size distributions for the six calcined limes. The size distribution curves are drawn for the assumption of complete pore filling. The arrows pointing left indicate the shift of the curves to meet the assumption of no pore filling ($\rho = \rho_0 (1 - \epsilon)$). For the Multifex precalcine, an arrow is shown also pointing to the right. This was drawn in because of an uncertainty in the porosity of the material (see Appendix E). In every case it is apparent that the uncertainties are small.

The particle size distribution for raw hydrate and carbonate sorbents are shown in Figures D-4 through D-8. These materials were prepared by aerodymanic classification, respectively, from Linwood atmospheric hydrate and Vicron 45-3.

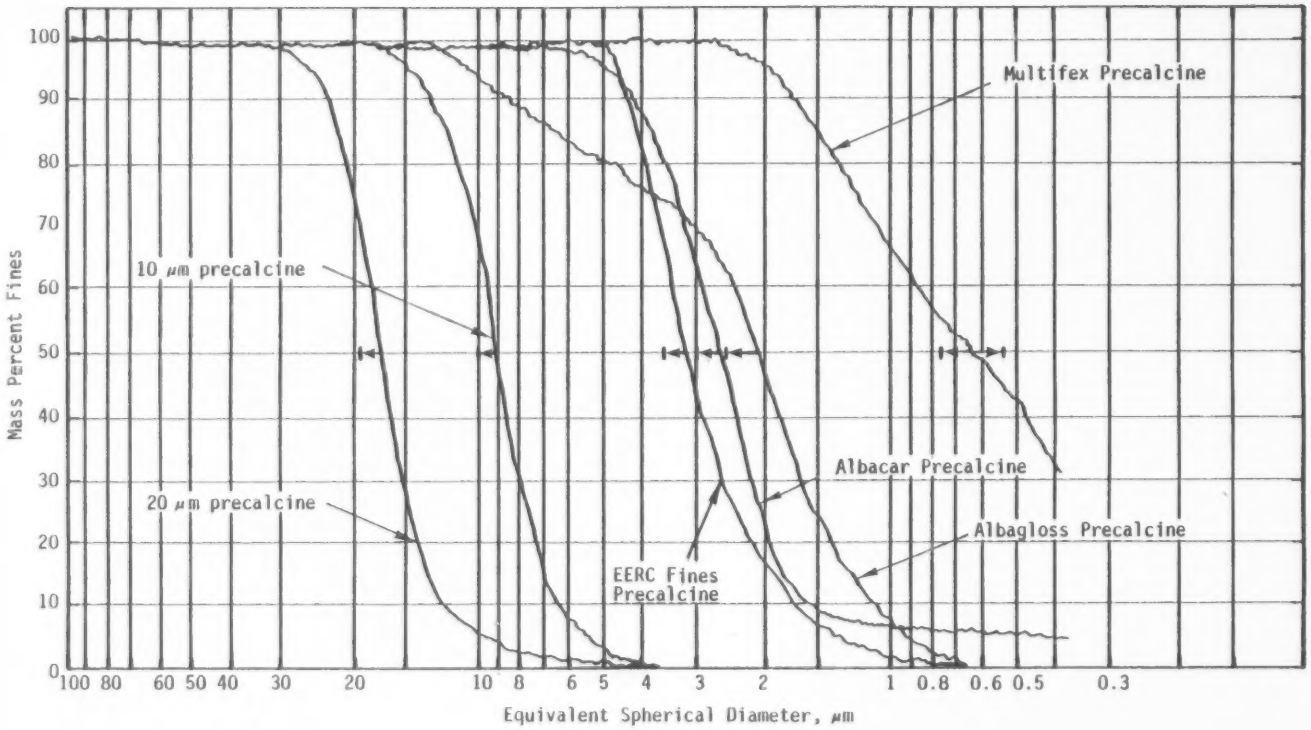

Figure D-3. Sedigraph particle size distributions for precalcined sorbents. The range of uncertainty, based on porisimetry analyses, is indicated by the arrows at the mean diameter for each material.

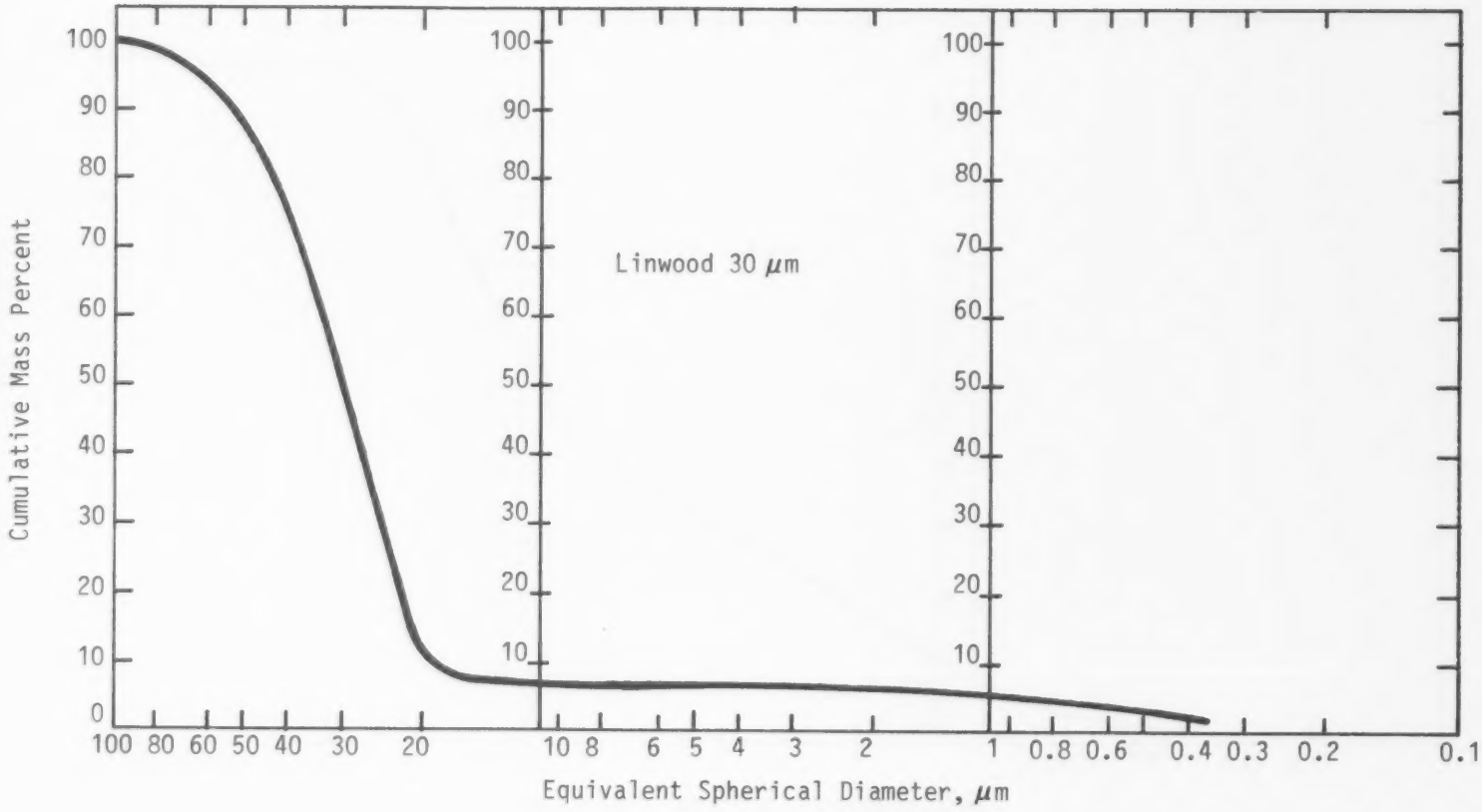

Figure D-4. Particle size distribution for 30 μm aerodynamically classified Linwood atmospheric hydrate.

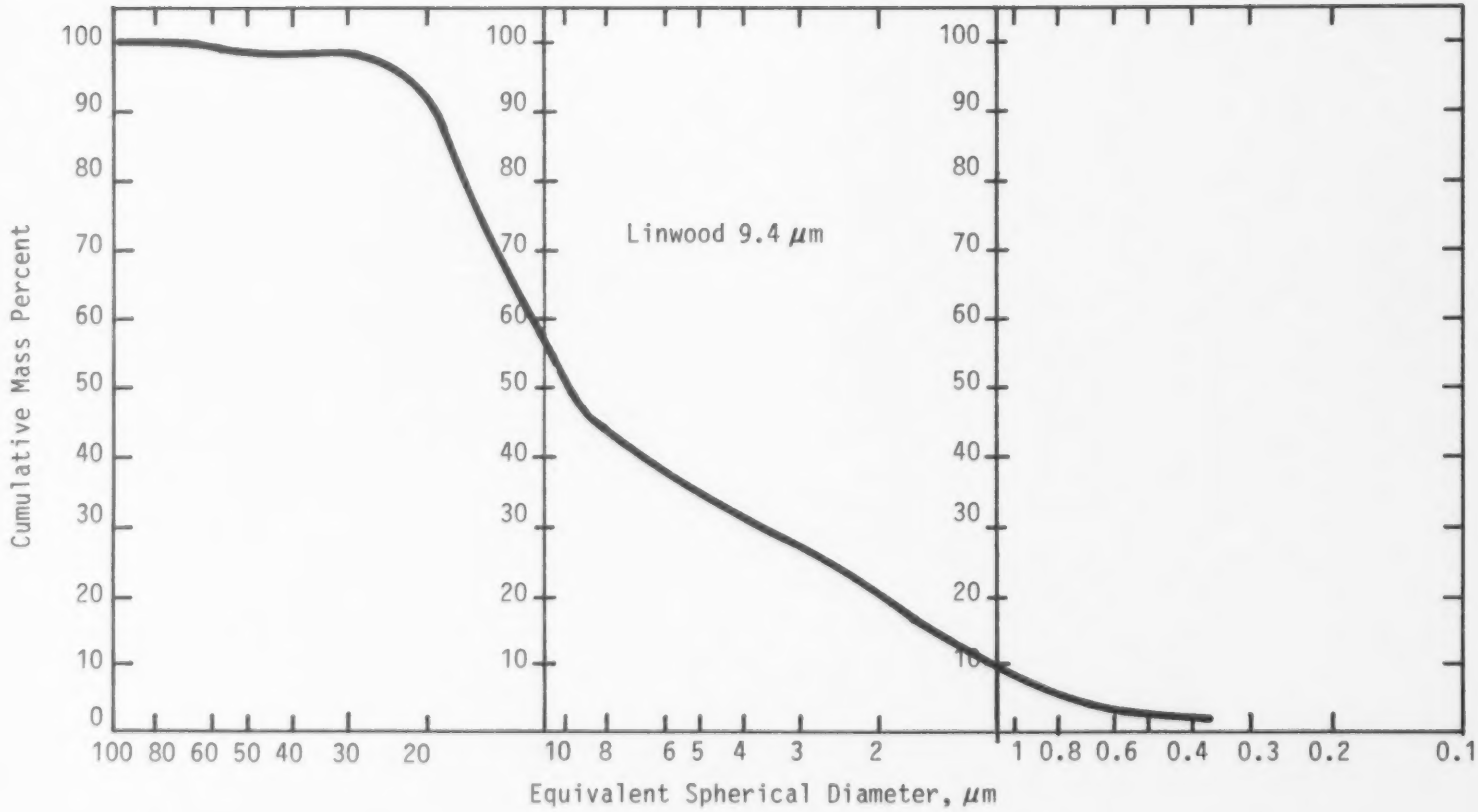

Figure D-5. Particle size distribution for 9.4 μm aerodynamically classified Linwood atmospheric hydrate.

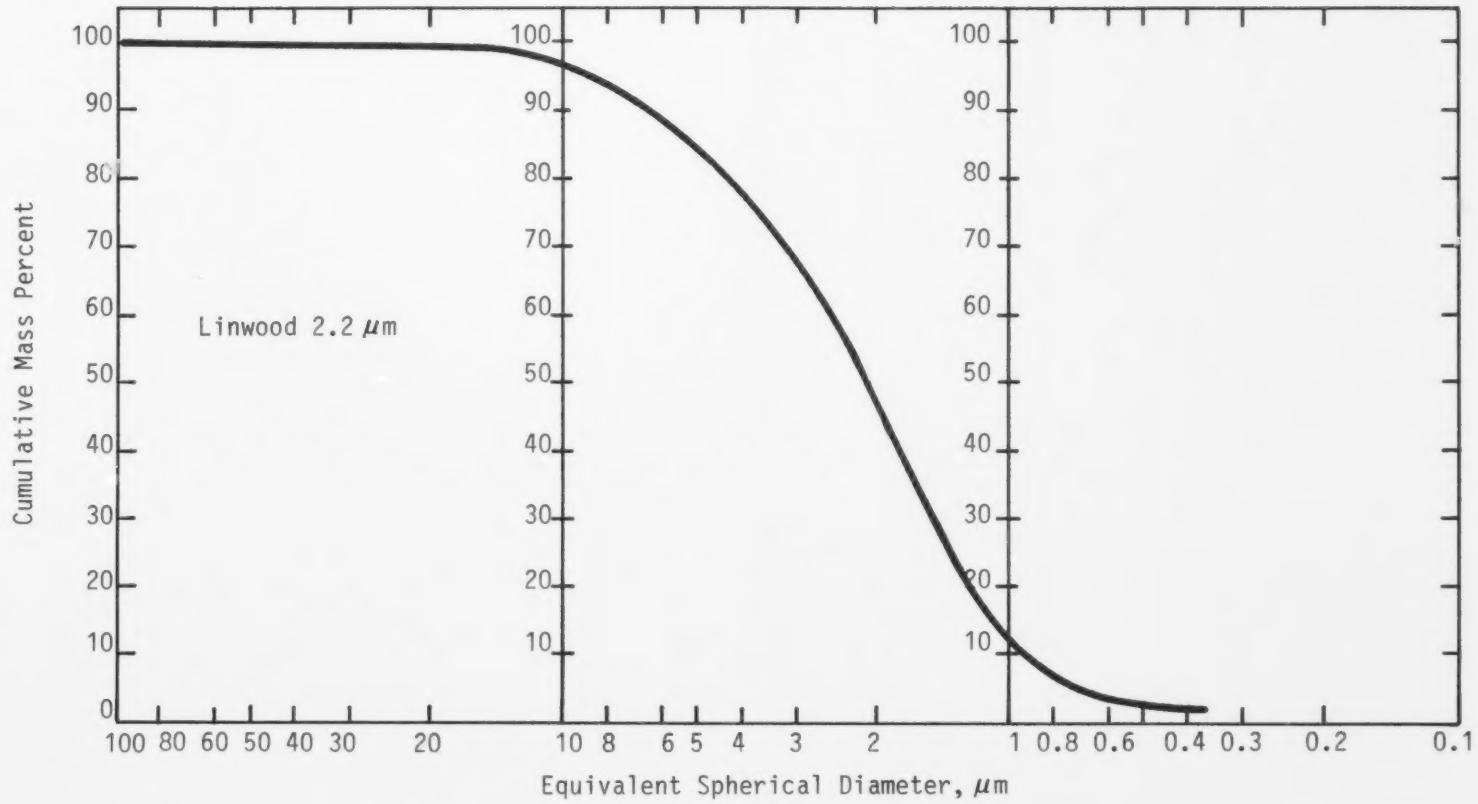

Figure D-6. Particle size distribution for 2.2 μm aerodynamically classified Linwood atmospheric hydrate.

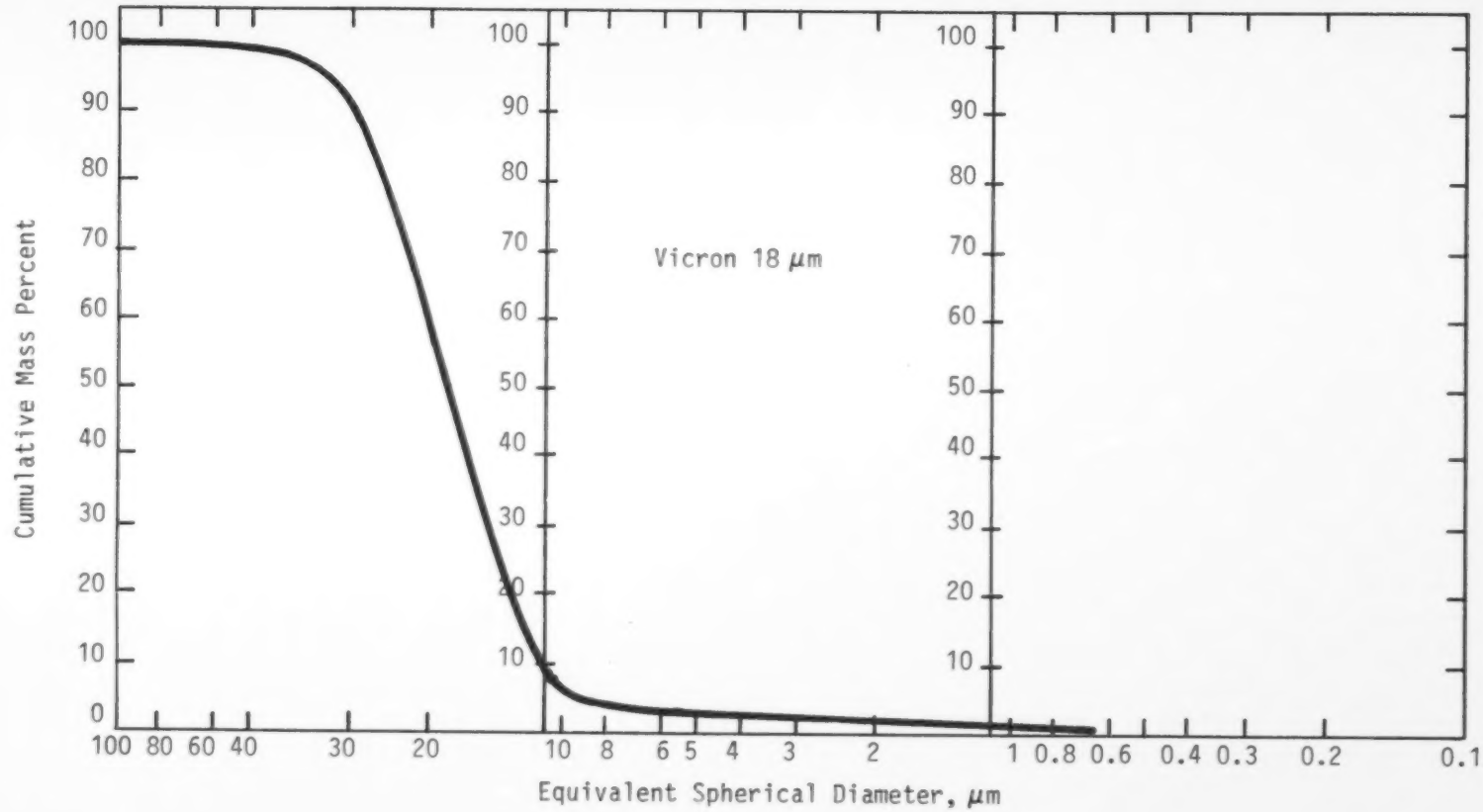

Figure D-7. Particle size distribution for 18 μm aerodynamically classified Vicron.

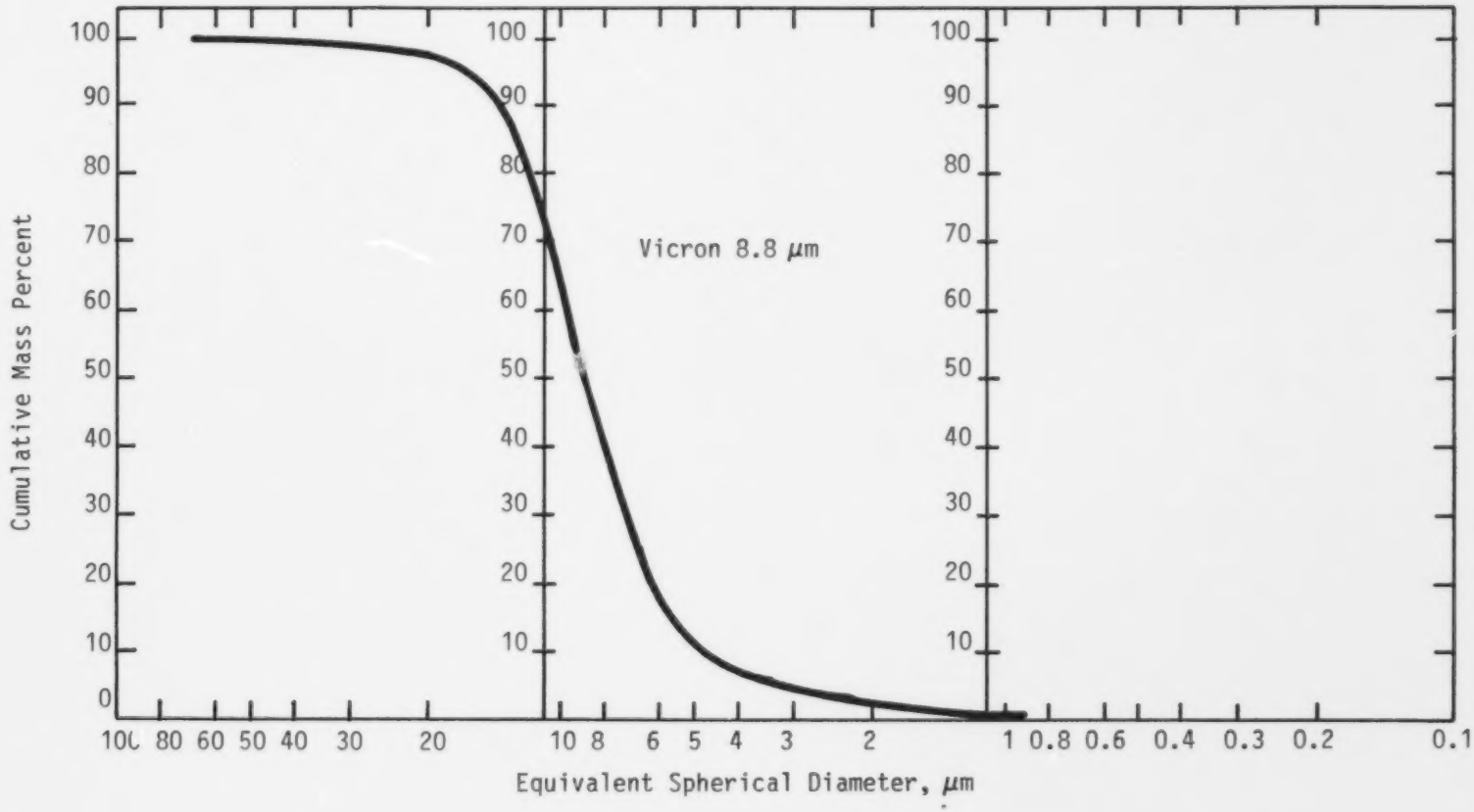

Figure D-8. Particle size distribution for 8.8 μm aerodynamically classified Vicron.

APPENDIX E

POROSIMETRY DATA

APPENDIX E
PORISIMETRY DATA

Pore size distributions measured by mercury intrusion porisimetry are provided for all eight of the precalcined sorbents in Figures E-1 through E-8. For three of the precalcines, the 20 micron (27 m^2/g), 10 micron (32 m^2/g), and the Multifex (25 m^2/g) nitrogen absorption porisimetry measurements are also shown, courtesy of Micromeritics Instrument Corporation. The curves shown in all of the figures were obtained by numerically differentiating the cumulative pore volume (obtained directly during the analyses) with respect to the naperian logarithm of the pore diameter.

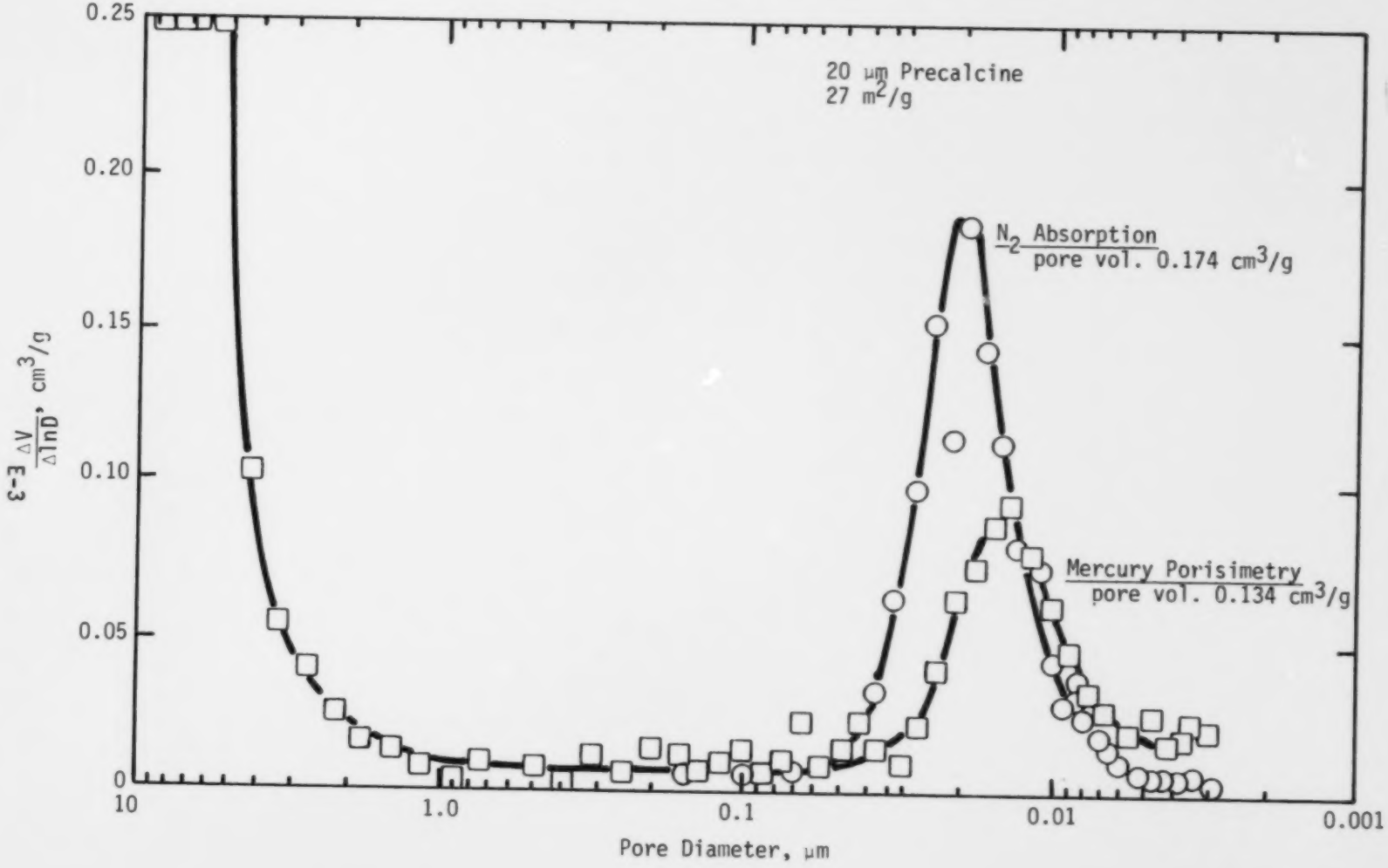

Figure E-1. Mercury-intrusion and nitrogen-absorption porisimetry curves for a 20 μm, 27 m^2/g precalcined lime.

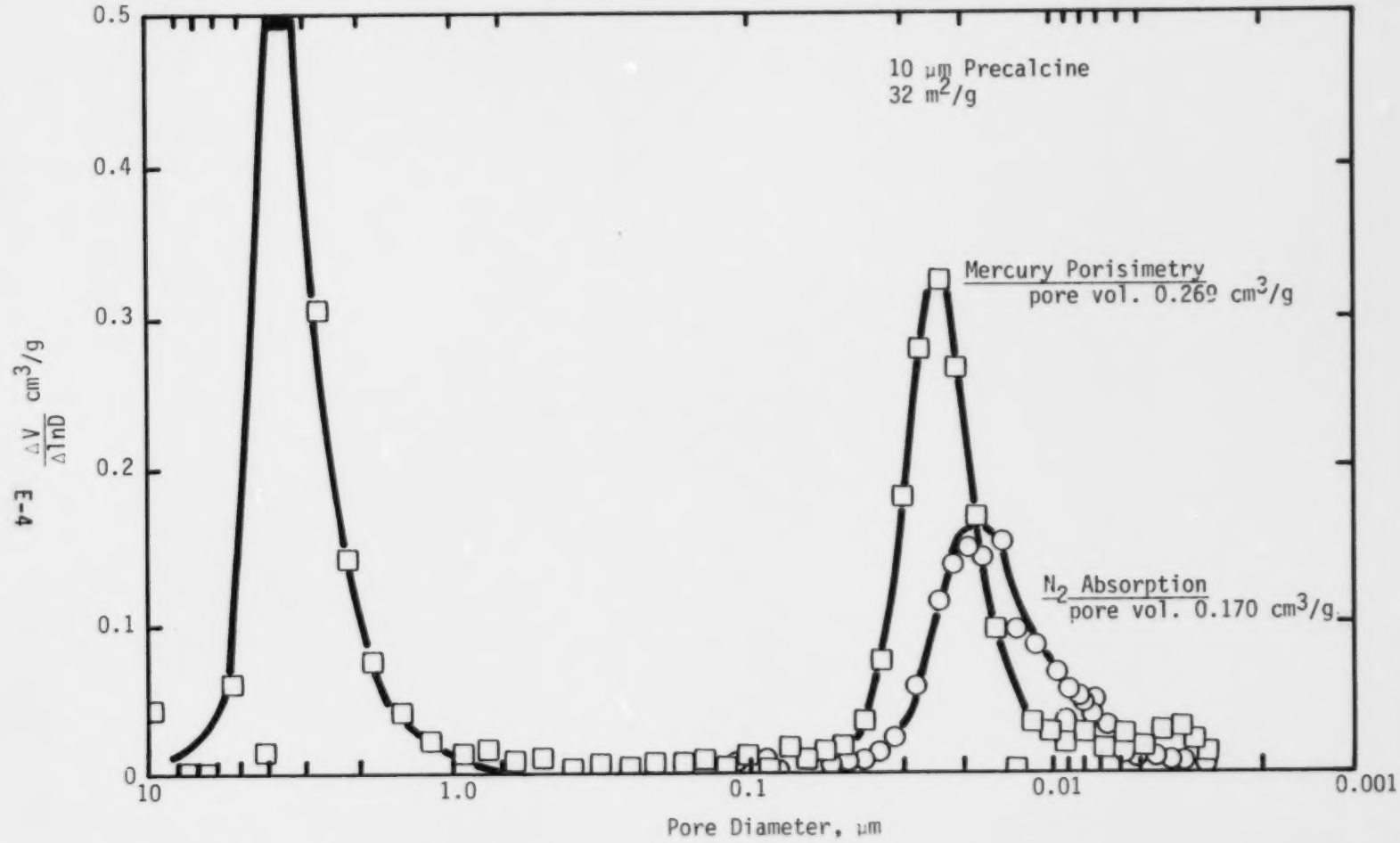

Figure E-2. Mercury-intrusion and nitrogen-absorption porisimetry curves for a 10 μm, 32 m^2/g precalcined lime.

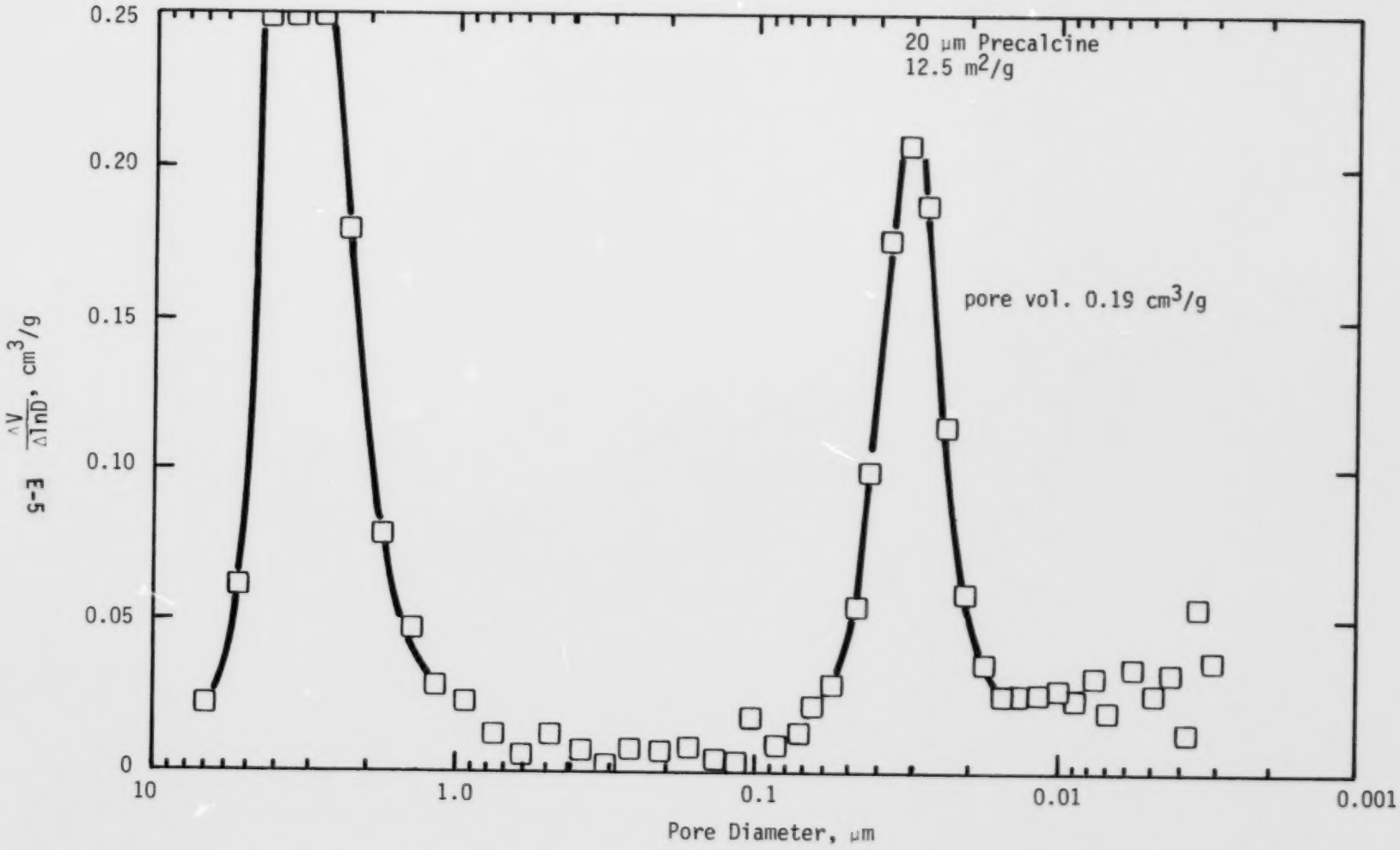

Figure E-3. Mercury-intrusion porisimetry curve for a 20 μm, 12.5 m^2/g precalcined lime.

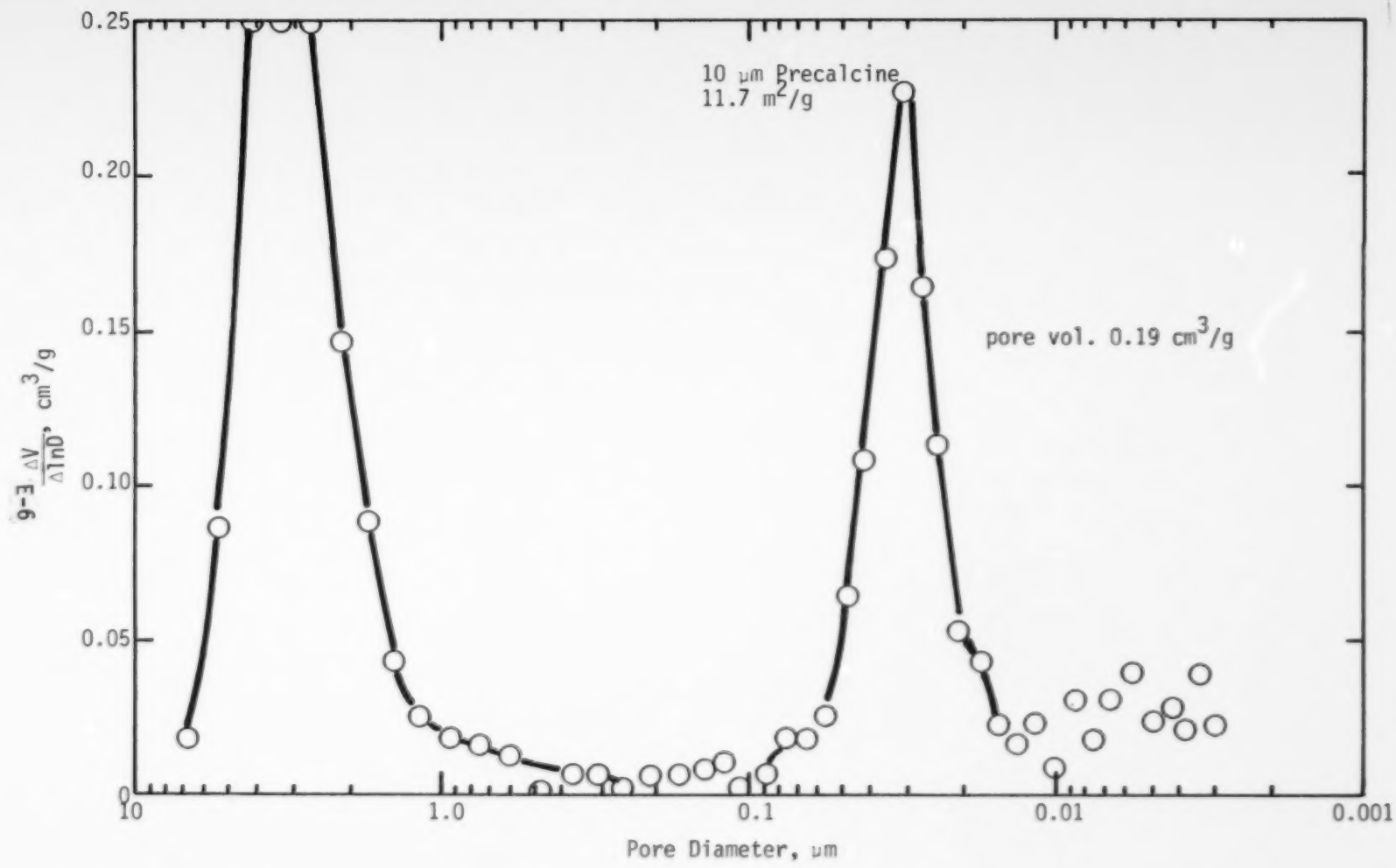

Figure E-4. Mercury-intrusion porisimetry curve for a 10 μm 11.7 m^2/g precalcined lime.

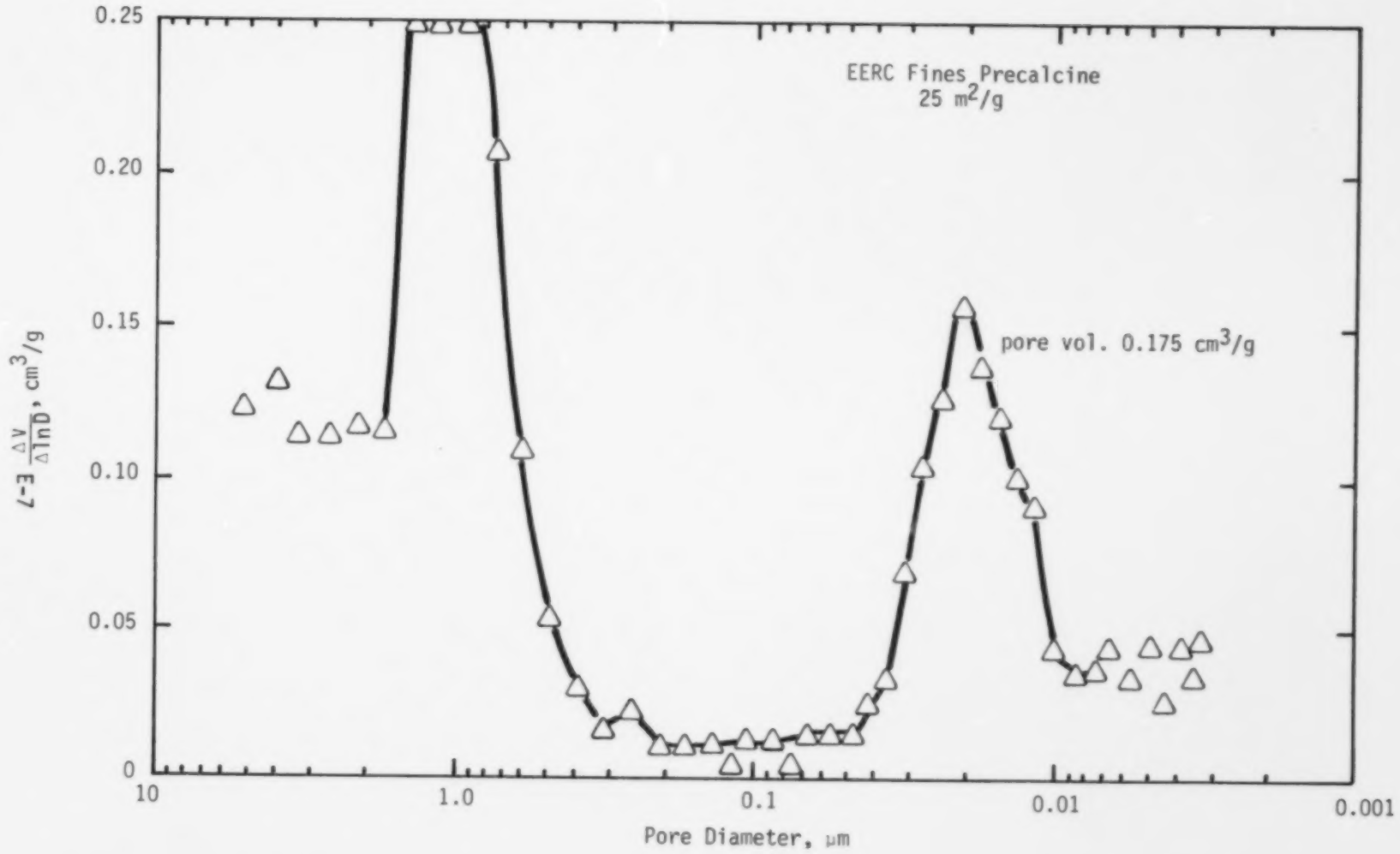

Figure E-5. Mercury-intrusion porisimetry curve for EERC fines precalcined lime.

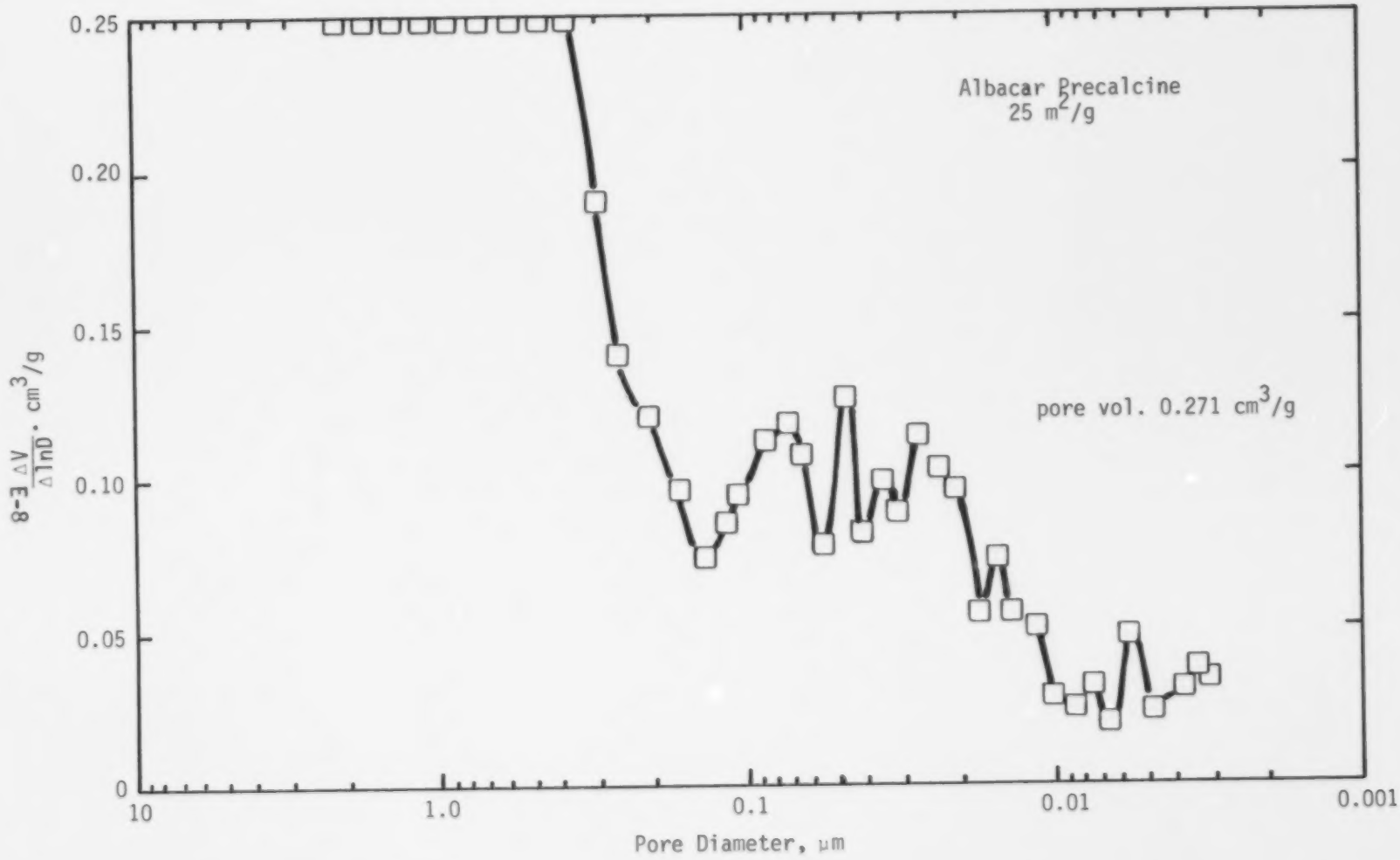

Figure E-6. Mercury-intrusion porisimetry curve for Albacar precalcined lime.

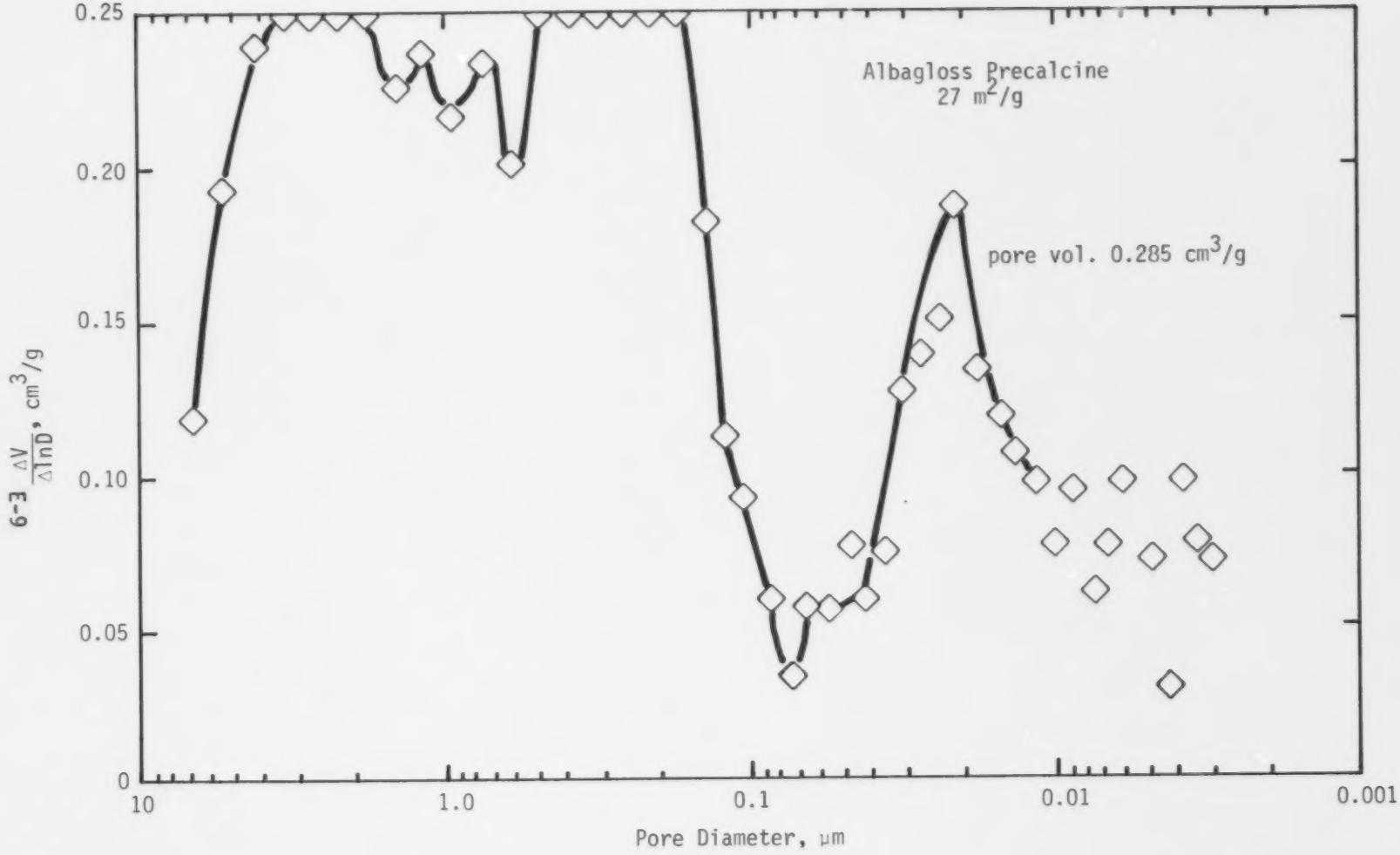

Figure E-7. Mercury-intrusion porisimetry curve for Albagloss precalcined lime.

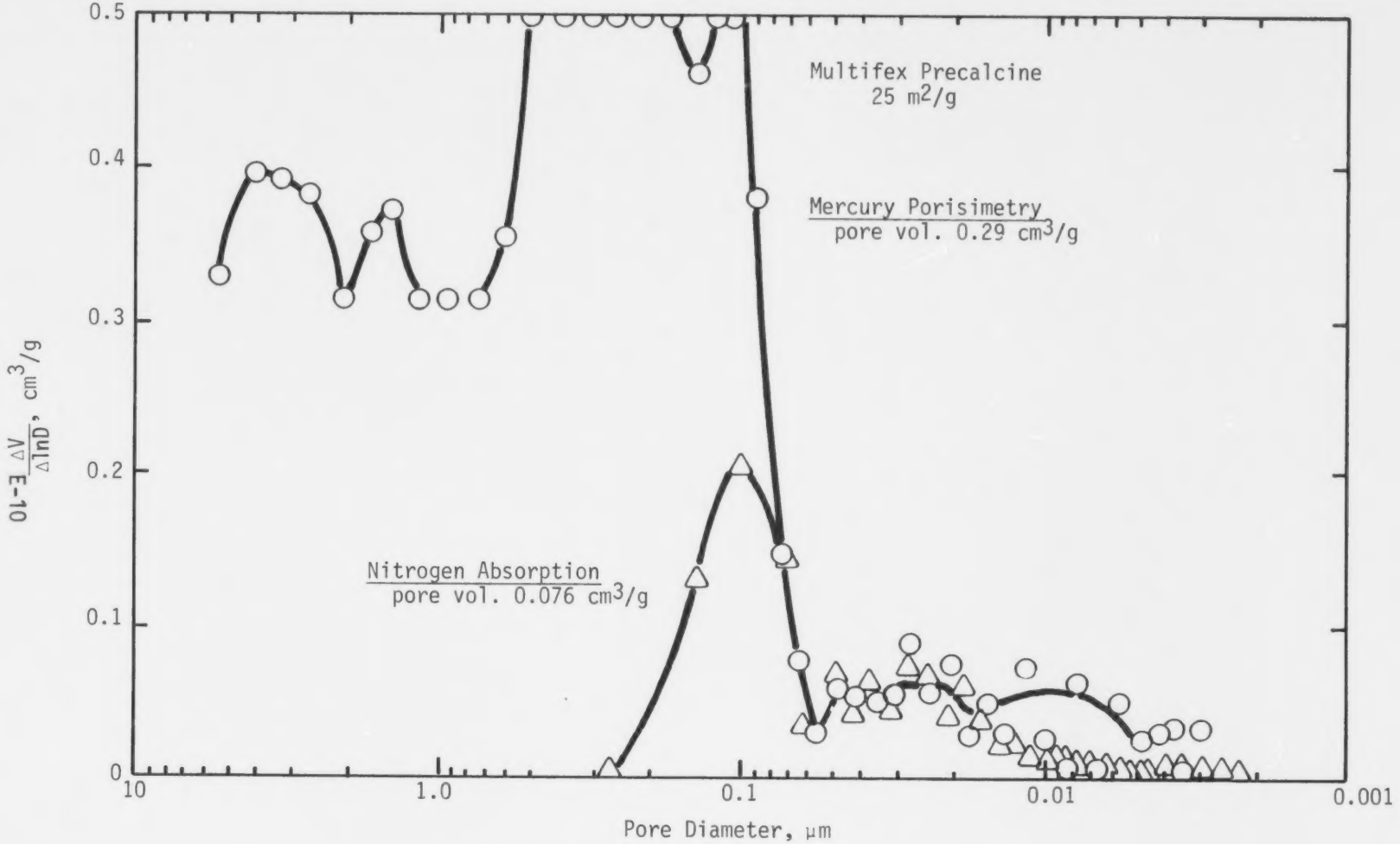

Figure E-8. Mercury-intrusion and nitrogen-absorption porisimetry curves for multifex precalcined lime.

APPENDIX F

QUALITY CONTROL EVALUATION REPORT

APPENDIX F
QUALITY CONTROL EVALUATION REPORT

Data quality objectives for critical measurements (which were listed in the approved QAPP) were met for all but one analysis - for which insufficient data were collected to permit precision instruments. The results are summarized in Table F-1. Data to support the reported precision and accuracy in Table F-1 are found in Tables F-2 through F-6. Excepting the temperature measurements, these represent the regular, periodic check of analytical procedures through analysis of standard materials over the course of this program.

With regard to the temperature measurements, the stated precision and accuracy are somewhat artificial. It must be recognized that these were "set" conditions. When the measured temperature was not within the stated goals, it was changed. Therefore no data were taken, or samples collected except within the stated limits of error for the designated temperature.

The results obtained in this study were intended as input to process model development. Therefore, every attempt was made to present the data and the experimental conditions in as straightforward a manner as possible. The quality of the data and their representativeness cannot be judged a priori since they are experimental in nature and have no "standard" against which to compare. Rather, the end user must decide, based on the appearance of the data, and the other information provided, whether these results are suitable for his own purposes. For interested readers discussion of the critical measurements listed in Table F-1 is provided in the following sections.

F.1 Perkin-Elmer 240B

The Perkins-Elmer 240B elemental analyzer was used to determine the water and carbonate contents of solid samples collected in this program. These samples were obtained both for sulfation studies as well as for surface area measurements. The evolved CO_2 and H_2O are reported as percent carbon and percent hydrogen, and will also include any organic material present

TABLE F-1. SUMMARY OF DATA QUALITY OBJECTIVES AND ACHIEVEMENT FOR CRITICAL MEASUREMENTS

Measurement	Reference	Precision (RSD[1])		Accuracy		Completeness	
		Goal	Achieved	Goal	Achieved	Goal	Achieved
Carbon (Perkin-Elmer 240B)	Instrument Instruction Manual	2%	0.3%	2%	0.3%	90%	100%
Hydrogen (Perkin-Elmer 240B)	Instrument Instruction Manual	5%	1.2%	5%	1.9%	90%	100%
Sulfur (Leco SC32)		10%	4.2%(5.5%)[2]	10%	2.4%(0.55%)[2]	90%	100%
Calcium	ASTM D2795	10%	1.0%	10%	0.2%	90%	100%
Specific surface area (Brunauer, Emmett, Teller)	Instrument Instruction Manual	10%	3.5%	20%	8.6%	100%	100%
Particle size distribution (X-ray sedimentation	Instrument Instruction Manual	20%	----	----	----	100%	100%
Reactor gas temperature (Fine wire thermocouple and readout, type S)	Omega 1984 Temperature Handbook	5%	1%	5%	5%(1%)[2]	70%	100%
Calcination system temperature (type K thermocouple)	Omega 1984 Temperature Handbook	5%	5%	5%	5%	90%	100%
Reactor wall temperature	Instrument Instruction Manual	5%	5%	5%	5%	100%	100%

[1] Relative standard deviation

[2] See discussion

TABLE F-2. PERKIN ELMER 240B ACCURACY AND PRECISION DATA

Carbon and Hydrogen Analysis

Standard: 2,5-Bis (4-Biphenylyl)oxazole			
86.84% C		5.13% C	
Carbon		Hydrogen	
Meas.	Pct. Dev.	Meas.	Pct. Dev.
86.62	-.253	5.17	.78
86.80	-.046	5.20	1.36
86.52	-.368	5.17	.78
86.47	-.426	5.17	.78
86.45	-.449	5.19	1.17
87.02	.207	5.26	2.53
86.65	-.219	5.25	2.34
86.75	-.104	5.33	3.90
86.42	-.484	5.15	0.39
86.08	-.875	5.24	2.14
86.69	-.173	5.21	1.56
86.59	-.288	5.28	2.92
86.05	-.910	5.15	0.39
86.61	-.265	5.24	2.14
86.75	-.104	5.25	2.34
85.66	-.207	5.31	3.51
86.80	-.046	5.30	3.31
x=86.58	x -0.295	x=5.23	x 1.90
SD= 0.25	$\pm$ 0.283	SD=0.06	$\pm$ 1.11

TABLE F-3. LECO SC32 PRECISION AND ACCURACY DATA

3.00% Sulfur Coal		10.00% Sulfur in $CaSO_4/CaCO_3$	
Meas.	Pct. Dev.	Meas.	Pct. Dev
3.05	1.67	10.00	0
3.20	6.67	9.93	- 0.7
3.24	8.0	10.00	0
2.90	- 3.33	9.93	- 0.7
2.92	- 2.67	9.01	- 9.9
2.94	- 2.0	8.13	-11.7
2.96	- 1.33	10.50	5.0
2.99	- 0.33	10.40	4.0
3.06	2.0	9.86	- 1.4
3.07	2.33	9.72	- 2.8
3.24	8.0	10.30	3.0
3.22	7.33	9.84	- 1.6
3.18	6.00	10.60	6.0
3.16	5.33	9.95	- 0.5
3.13	4.33	9.97	- 0.3
3.11	3.67	10.00	0
3.14	4.67	9.43	- 5.3
3.15	5.00	10.00	0
2.83	- 5.67	10.20	2.0
2.84	- 5.33	10.40	4.0
3.09	3.00		
3.12	4.00	x= 9.91	0.55 $\pm$ 4.45
3.11	3.67		
2.88	- 4.00	SD= 0.55	
2.89	- 3.67		
2.85	- 5.00		
2.90	- 1.33		
2.92	- 2.67		
3.03	1.0		
3.06	2.0		
3.32	10.67		
3.26	8.67		
3.20	6.67		
3.18	6.00		
3.14	4.67		
3.11	3.67		
3.09	3.00		
3.01	0.33		
3.20	6.67		
3.16	5.33		
3.03	1.00		
x=3.07	2.39%		
SD=0.13	$\pm$4.26		

TABLE F-4. PRECISION AND ACCURACY DATA FOR CaO ANALYSIS
(Modified ASTM D2795 - from Shawnee Test Procedures Manual. April 1985)

Reagent Grade $CaCO_3$ 56.08% as CaO	
Meas.	Pct. Dev.
56.52	0.75
56.58	0.89
53.36	0.50
55.81	-0.48
55.89	-0.34
55.95	-0.23
55.73	-0.62
55.90	-0.32
55.83	-0.45
56.00	-0.14
56.80	1.28
57.01	1.66
55.82	-0.46
56.44	0.64
55.93	-0.27
56.93	1.52
55.15	-1.66
55.88	-0.36
55.23	-1.52
55.38	-1.25
54.85	-2.19
55.49	-1.05
55.35	-1.30
56.05	-0.05
56.52	0.78
56.17	0.17
56.35	0.48
55.99	-0.16
56.37	0.52
55.36	-1.25
56.28	0.36
55.80	-0.50
56.00	-0.14
55.40	-1.21
55.56	-0.93
55.86	-1.39
x=55.96	x=-0.21
SD= 0.51	$\pm$ 0.90

TABLE F-5. PRECISION AND ACCURACY DATA FOR BET SURFACE AREA ANALYSIS

29.8 m^2/g Standard	
Meas.	Pct. Dev.
26.7	-10.4
26.1	-12.42
28.3	- 5.03
26.4	-11.41
27.8	- 6.71
28.5	- 4.36
26.9	- 9.73
x=27.2	- 8.58%
SD= 0.95	± 3.2 %

TABLE F-6. TYPICAL DATA FOR TEMPERATURE VARIATIONS WITHIN THE ISOTHERMAL REACTOR

Nominal 1000°C Condition	
Measured Temperature	Pct. Dev.
998	- .20
1010	1.00
1014	1.40
1014	1.30
1010	1.00
1008	.800
1006	.600
998	- 200
1010	1.00
1009	.900
1010	1.00
1010	1.00
1009	.90
1005	.50
1000	.00
993	.700
x=1006	x = .64
SD=6.03	± .60

(generally nil in limestone samples). Standards for the instruments are organic compounds provided by the instrument manufacturer. While these standards do not resemble the typical samples analyzed in the instrument, they provide very accurate checks on the instrument accuracy and sensitivity. The results listed in Table F-2 are for 2,5-Bis(4-Biphenylyl)oxazole. The standard checks were performed on a weekly basis throughout the program.

F.2 Leco SC32 Sulfur Analyzer

The Leco SC32 was employed to determine the sulfur content of sulfated samples. Two approaches were used on a regular periodic basis to determine precision and accuracy of the measurement. These are outlined in Table F-3. The principle use of the instruments in house is in measuring sulfur content of ash and char samples. Therefore, a manufacturer-supplied coal standard is employed. Because of application to measuring sulfur in sorbent samples, in-house-generated "standards" are prepared from reagent-grade $CaSO_4$ and $CaCO_3$ and tested regularly. These results also are shown in Table F-3.

F.3 Calcium Determination

Calcium determination for sorbent samples were performed following a modification to ASTM D2795 as outlined in the Shawnee Test Procedures Manual (April 1985). The standard for this analysis was a Baker Analyzed reagent grade $CaCO_3$. Standard test data are shown in Table F-4.

F.4 BET Specific Surface Area Measurements

Specific surface area measurements were performed by the BET method of N_2-adsorption isotherm analysis. A Quantachrome Quantasorb unit was used for the measurements. The standard employed for the accuracy and precision checks was a 29.8 m^2/g sample of porous Al_2O_3. The standard was certified by quantachrome for the N_2-absorption method. Precision of the measurements has been quite good although the average has remained about 10% low. The sample was re-analyzed by Quantachrome as a blind check and their results fell within our standard deviation. As a result it appears likely that the real

accuracy of these measurements is better than the value cited in Table F-1. The standard analysis data for the N_2-BET measurements are shown in Table F-5.

F.5 Particle Size Analysis

Particle size was determined by a cross section of methods, but relied ultimately on X-ray sedimentation using a Micromeritics Sedigraph Analyzer. Other methods were aerodynamic classification and scanning electron microscopy. The basis for X-ray sedimentation is a model of each particle as a sphere falling through a fluid at its terminal velocity. The equivalent spherical diameter of a particle is defined as the diameter of a sphere with the same apparent density which would fall at the same rate in the fluid. Numerous tests have been performed by the manufacturer using, e.g., NBS standard glass spheres of various sizes. All of these affirm the accuracy of the technique under near perfect conditions. Real materials such as those studied here provide a challenge to particle size measurement techniques. Interferences such as agglomeration of particles, interpretation of non uniform shapes as spheres, and uncertainties in the apparent porosity must be taken into account. The reader is cautioned to consider these factors when referring to the particle size data shown in this report. A discussion of uncertainties due to pore filling of porous materials is given in Appendix D. Replicate analyses of samples were not performed during this program, therefore no precision (repeatability) data were obtained.

F.6 Reactor Temperature Measurements

Reactor temperature measurements were made using Type-S (Pt/Pt-10% Rh) bare-wire thermocouples. These thermocouples were not calibrated but were manufactured from thermocouple-quality matched wires. Because bare-wire thermocouples can deteriorate rapidly under severe or corrosive conditions, several were kept on hand and were cross-compared regularly. Table F-6 provides data which represent the uniformity and repeatability of the reactor temperature measurements.